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AUTHOR - AUTEUR

Full Name of Author - Nom complet de l'auteur

WILLIAM ALEXANDER MILNE-HOME

Date of Birth - Date de naissance

1943-10-25

Canadian Citizen - Citoyen canadien

☐ Yes / Oui

☒ No / Non

Country of Birth - Lieu de naissance

TRINIDAD & TOBAGO

Permanent Address - Résidence fixe

c/o GREY, BOX 32,
BANGALOW, NSW 2479
AUSTRALIA

THESIS - THÈSE

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Name of Supervisor - Nom du directeur de thèse

DR. F. W. SCHWARTZ

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Modelling Mass Transport in Clastic Sands and Sandstones

by



William Alexander Milne-Home

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF Doctor of Philosophy

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W.A. Milne-Home

PERMANENT ADDRESS:

c/o Grey Box 32
Bangalore, NSW 2479
Australia

DATED 25th September 1985

THE UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled Modelling Mass Transport in Clastic Sands and Sandstones submitted by William Alexander Milne-Home in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

.....*Frank W. Schwartz*.....

Supervisor

.....*Fred J. Krystoff*.....

.....*James D. Dyer*.....

.....*Dirk Jackson*.....

External Examiner

Date *25th September 1985*

ABSTRACT

The prediction of contaminant migration in a porous medium requires the estimation of its intrinsic properties of porosity, permeability and dispersivity. These properties must be coupled with estimates of the fluid characteristic within the flow domain to obtain measures of the hydraulic conductivity and dispersion tensors of the porous medium. In addition it is necessary to determine the cation exchange capacity (CEC) of the porous medium for contaminants which react with the medium through ion exchange. Empirical expressions which relate these properties to the grain size parameters and mineralogy of clay- and silt- rich sands and sandstones have been developed from existing relationships for "clean" sands and sandstones.

The porosity of clay- and silt- rich sands is found to be controlled by the uniformity coefficient, the amount of silt- sized material and the ratio of the largest to the smallest grain size. The specific surface of the aggregate can be estimated from particle shape coefficients applied to the mass and mean diameter of the particles forming each size fraction. This value of the specific surface is used in conjunction with porosity to calculate the permeability. The particle shape coefficients are determined from the surface area- to- volume- ratios of the particles; the mineralogy of the sediment governs the overall shape coefficient of each size fraction. The dispersivity of these sands can be described by the uniformity coefficient and the mean grain

size of the sediment. In clastic sandstones dispersivity is an intrinsically linear function of the porosity, permeability and formation factor. The cation exchange capacity of all these media can be predicted from knowledge of the specific surface, or it may be found from the mineralogical composition of the finer sized fractions of the sands or from the authigenic mineralogy of sandstones.

The sensitivity of the mass transport parameters is demonstrated by calculating them for various combinations of grain size, sorting and clay mineralogy of simulated sediments. These simulations show that the porosity, permeability and dispersivity of sands and silts with small amounts of clay are more strongly affected by variations in grain size and sorting than clay mineralogy; the opposite is true for the CEC.

An extant "method- of- characteristics" (MOC) numerical model for the simulation of mass transport in steady, one dimensional and two- dimensional flow domains has been extended and modified to include the effects of ion exchange on the concentration of a tracer cation in the solute. This model has been verified by comparison with well- known analytical solutions to the one- dimensional and two- dimensional transport equation for simple boundary and initial conditions. The model is used to demonstrate the effects of grain size and pore mineral composition on the movement of a tracer in the simulated silty sands described previously. Finally the utility of the MOC and parameter

generating models is demonstrated by their application to the simulation of mass transport in sections through the Milk River Formation of Southern Alberta, the Oxnard aquitard of California and the Muddy Formation of Montana and Wyoming.

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1. INTRODUCTION

1.1 Statement of the Problem

One of the major concerns of contemporary hydrogeology is the prediction of the physical and chemical transport of solutes in geological porous media. Mass is transported in flowing groundwater as a consequence of physical and chemical processes which act to influence the distribution of the solutes in space and time. Mass transport is described by the advection-dispersion equation, (Pinder and Bredehoeft, 1967; Bear, 1972). Its most general formulation is

$$\begin{aligned}\partial(nC_i)/\partial t = & \partial/\partial x[nD_{xx}(\partial C_i/\partial x) + nD_{xy}(\partial C_i/\partial y)] \\ & + \partial/\partial y[nD_{yx}(\partial C_i/\partial x) + nD_{yy}(\partial C_i/\partial y)] \\ & - [\partial(v_x C_i)/\partial x] - [\partial(v_y C_i)/\partial y] \\ & + \sum_j R_{ij}\end{aligned}\quad (1)$$

Schwartz (1984)

where

C_i = concentration of the i th constituent

n = porosity

t = time

D = dispersion tensor

v = Darcy velocity

R_{ij} = reaction term describing the rate of production of the i th constituent in j reactions

$\sum_j$ = Sum from $j=1$ to $j=m$

x, y = Cartesian coordinates

In this equation the dispersion coefficients, Darcy velocity, porosity and coefficients built into the various reaction terms are transport parameters related to the geologic and hydrogeologic setting. In practical applications, accurate and physically realistic solutions to (1) are dependent on good estimates of these parameters. These parameters can be measured in the laboratory or in the field. However these direct methods are often technically and/or economically unfeasible, and the parameters must be determined by indirect means.

The indirect approach is to estimate the required parameters of (1) from various constitutive characteristics of the the porous medium. In the case of clastic sediments, characteristics such as the distribution of the sizes of component grains, the shapes of the grains and the texture of the aggregate can be related to the porosity, permeability and, in conjunction with fluid velocity, the dispersivity of the medium. The composition and morphology of the pore- lining authigenic minerals of clastic sedimentary rocks control the hydraulic and transport characteristics of these media.

A considerable body of experimental work in these areas exists for those classes of porous media which include clastic sands and sandstones with small to negligible quantities of silt- and clay- sized material (the "clean" sands of petroleum engineering terminology)..A similar body of knowledge has been accumulated for the chemical and

physical behaviour of soils. Nevertheless, a need is perceived for the extension of these constitutive relationships to sands which contain a significant proportion of silt and clay, and to sandstones rich in authigenic clay minerals. It is necessary, also, to examine the effects of clay minerals in these media on the cation exchange properties of the media. The goal of this synergism is to allow the construction of geologically realistic simulations of mass transport in these classes of porous media, as noted by Schwartz (1977).

Consequently, the following objectives were set out for this study:

- (a) to examine the relationships between the grain size distribution of clastic sands, on the one hand, and the mineralogy of clastic sandstones and the porosity, permeability, dispersivity and CEC of all such media;
- (b) to modify these relationships for application to silty sands and clay - rich sandstones;
- (c) to develop new relationships for these media as necessary;
- (d) to use these relationships to predict the hydraulic and transport parameters of clastic sands and sandstones, respectively from their lithology and mineralogy;
- (e) to develop a model of ion exchange for simulating mass transport in these classes of porous media.

The application of these objectives is to demonstrate the effects of varying the lithology and mineralogy on the

transport properties of simple but realistic simulated clastic sands. Further applications are to the simulation of mass transport in actual geological cross - sections for which estimates of the porosity, permeability, dispersivity and CEC are obtained by the techniques developed in this study.

The remainder of this section is concerned with a review of the geology, clay mineralogy and hydrogeology of clay- rich clastic sands and sandstones. This descriptive framework will place the subsequent discussion of the physical and chemical constitutive relationships in a geological perspective.

1.2 Geology and Clay Mineralogy of Clastic Sands and Sandstones

Clastic sediment in its broadest sense is loose, non-cohesive, particulate material from diverse geologic parent materials which has been disaggregated by various geologic processes. Sediment is classified on the Wentworth scale into classes based on specified size ranges; of these, only *sand* through *clay* sediments are considered herein. The bulk mineralogy and chemical composition of a sediment reflects the nature of the parent material. The environment of deposition controls the distribution of minerals within the mass of sediment; Griffiths (1966).

The distribution of clastic sands and sandstones, their spatial continuity and structural characteristics, result

from their environment of deposition. A large body of work by sedimentologists has resulted in the development of broad criteria for the recognition of depositional environments. Microscale properties of a sediment such as mode of packing of grains, grain shape and size distribution govern the occurrence of minerals within the fabric of the sediment. Kezdi (1979) and Kovacs (1981) have shown how the mineralogy of a sediment correlates with its grain size distribution, such that clay minerals, colloids and organic matter are concentrated into the finer sized fractions. These fractions because of their physical and chemical properties play an important part in mass transport in the solute phase within the pore space of sediments on both the microscopic and the macroscopic scales.

Tables 1 and 2 list the minerals which have been observed to occur in clastic sands and sandstones. The term "illite" includes clay-sized micas, but following Reesman and Keller (1967) and Weaver and Pollard (1973) the usage herein is confined to reference illites of the API definition. From the standpoint of mass transport the most important minerals are the clays, although the micas, goethite and hematite also play a significant role in these processes. Excellent descriptions of the structure of clay minerals are to be found in Brindley (1981) and in Brown et al., (1978).

Detrital materials can be incorporated in a sediment at the time of deposition (*syndepositional*) or shortly after

TABLE 1. MINERALOGY OF ARENITES AND WACKES *

Concentration ≥10% of Rock	Concentration <10% of Rock	Concentration ≤1% of Rock
	(Detrital Minerals)	
Quartz ¹⁻³	Chert ¹⁻³	Zircon
Clay minerals ³	Coarse-grained	Tourmaline
Fine-grained	micas ¹⁻³	Epidote
micas ¹⁻³	Feldspars ¹⁻³	Garnet
		Hornblende ¹⁻³
		Ilmenite ¹⁻³
		Magnetite ¹⁻³
		Rutile ¹⁻³
	(Authigenic Minerals)	
Calcite	Chert	Anatase
Dolomite	Secondary silica	Feldspar
	and quartz	Mica
	Gypsum	Iron oxides
	Clay minerals	and hydroxides
	Glaucanite	

Common grain size:

- 1 = sand (.0625mm to 2.0mm)
- 2 = silt (3.9μm to 62.5μm)
- 3 = clay (<3.9μm)

Source: modified from Krumbein and Sloss (1963)

* Terminology after Pettijohn et al (1972) and Fuchtbauer (1974).

deposition by bioturbation and by mechanical infiltration. Wilson and Pittman(1977) describe the occurrence of detrital clays in sands and sandstones. The occurrence of detrital materials is summarised as follows:

- (a) *dispersed matrix*: simultaneous deposition of clay and silt-sized particles with coarser grains;
- (b) *intercalated laminae*: concentrations of clay and silt into distinct thin layers, often including organic materials;
- (c) *coarse particles*: mudstone and shale fragments and mud

"rip-up" clasts created by penecontemporaneous erosion of laminae; biogenic pellets; floccules showing "house-of-cards" structure, (Van Olphen, 1963; Collins and McGown, 1974); non-clay detritus;

(d) *burrow linings and fillings*: tubular deposits of clays and silt homogenized by organisms, and which cut across stratifications;

(e) *infiltration residues*: (Signor, 1973; Crone, 1974); these form:

- (i) flocculated aggregates filling void spaces;
- (ii) platelets lining surfaces of detrital grains;
- (iii) platelets perpendicular to surfaces of detrital grains.

Wilson (1982) shows how the mode of clay occurrence listed above can be related to the environment of deposition. It should be noted that these detrital clays can undergo *transformation*, i.e. modification without altering their basic 2-layer or 3-layer structure, (Milot, 1970), during weathering, sedimentation or burial diagenesis. Thus, illite and chlorite may be transformed reversibly to vermiculite, and chlorite similarly goes to mixed-layer chlorite/smectite.

Minerals can also be found within a pore or pore throat as a *lining* or as a *filling*. For example, the lithic arenites and lithic and feldspathic graywackes of the the Cretaceous and Tertiary of the Alberta Foothills and Plains contain detrital clay particles and are cemented by authigenic quartz, carbonates, zeolites and clay

TABLE 2. CLAY MINERALS IN SANDS AND SANDSTONES

Clay Mineral Group	Clay Minerals
Kaolinite	KAOLINITE halloysite dickite
Illite	"ILLITE" glauconite
Chlorite	CHLORITE clinochore corrensite
Smectite	MONTMORILLONITE beidellite nontronite hectorite
Vermiculite	VERMICULITE
Mixed-layer	illite-smectite montmorillonite-chlorite ILLITE-MONTMORILLONITE

The most commonly occurring mineral in each group is
CAPITALIZED

Sources: Carrigy and Mellon (1964); Almon et al (1976);
Boles and Franks (1979).

minerals, (Lerbekmo, 1961; Carrigy and Mellon, 1964). Table 3
condenses their observations of the authigenic clay minerals
in these sandstones.

Authigenic clay minerals appear to form the most common
pore linings and fillings in the majority of quartz-arenites
and feldspathic wackes. Wilson and Pittman (1977) found
authigenic clays in over 3000 sandstones of different types,
ages and depositional origins. They give summary
descriptions of the distribution and characteristics of the

TABLE 3. OCCURRENCE OF CLAY MINERALS IN SANDSTONES OF ALBERTA

Clay Mineral	Mode of Occurrence
Kaolinite	Intergranular, microcrystalline aggregates (pore fillings)
Illite	(a) intergranular microcrystalline aggregates similar to kaolinite (b) thin, fibrous aggregates growing outwards from pore walls (mainly in fine-grained, low-porosity sandstones)
Chlorite	Pore lining similar to Illite-(b) and, less commonly, Kaolinite. Often, Chlorite pore-linings have other minerals as fillings
Smectite	Pore lining similar to Kaolinite and Illite ; also as grains due to alteration of pre-existing minerals or rock fragments : Kaolinite & Chlorite coexist as cement

most common diagenetic minerals and present ways of distinguishing them from detrital clays. Authigenic clays are well crystallised and individual flakes and aggregates may grow to considerable size. Kaolinite and dickite form individual hexagonal flakes but as aggregates they occur as stacked plates or books some 2 to 2500 microns long, generally 2 - 20 microns. They may also occur as vermicular bodies some 10 - 2500 microns in length with 20 - 200 microns as a mean length. Also they make up sheets 0.1 - 1.0 micron in thickness. These minerals form pore fillings. Another pore-filling mineral, chlorite, forms equidimensional angular or lobate flakes which aggregate to rosettes 4 - 150 microns in length (generally 4 - 20

microns); chlorite also is found as fan shaped, fibrous bundles 8 - 40 microns in length. These forms of chlorite are seen both as pore fillings and pore linings whereas the individual pseudo-hexagonal and curled equidimensional forms and their aggregated plates and honeycomb structures 2 - 10 microns in thickness occur as linings. Illite laths, smectite sheets and honeycombs, and mixed-layer illite-smectite clays form linings about 2 - 12 microns thick.

Güven et al. (1980) report their findings with respect to the morphology of authigenic illite from various sandstone formations. Illite is seen to occur as crystalline laths up to 30 microns in length growing outwards from gel-like cores which form a dense coating on the pore walls. These illites ranged from pure to mixed-layer types.

Neasham (1977) presents a three-fold classification of the occurrence of dispersed clay in sandstones. Dispersed clays are found within the pore space in the forms listed below.

- (a) *Discrete particle fill*. Mainly kaolinite plates and books, forming discrete clusters scattered through the pore space.
- (b) *Pore-lining material*. Clays attached to pore walls in the form of a continuous lining 12 microns thick or greater. The clay crystals may be attached to the wall such that their long axis is either normal or parallel to it. In both cases considerable microporosity is developed. Illite, chlorite and montmorillonite display

this mode of occurrence.

- (c) *Pore-bridging material*. This class represents an extension of (b) to the extent of completely bridging the pore space. Illite, chlorite and montmorillonite have been observed to display this morphology. The interlocked, lath-like crystals create an extensive network of micropores, resulting in extremely tortuous conduits for fluid flow.

Wilson and Pittman (1977) describe non-clay minerals and mineraloids which also may line or fill pores. One example of this class is the amorphous aluminium hydroxide, chliachite, with habit and occurrence resembling chlorite or smectite. These authors also observed in some samples scattered grains 15 - 30 microns in diameter resembling kaolinite booklets under the SEM. However EDXRA showed the grains to contain only iron, and Wilson and Pittman (1977) interpret them as iron-oxide particles.

2. CONSTITUTIVE RELATIONSHIPS FOR MODELLING MASS TRANSPORT

2.1 Introduction

Among the terms of reference outlined for this study are the goals of modifying or developing relationships between the lithology and mineralogy of sands and sandstones and their mass transport properties. In this chapter those relationships are discussed for each parameter relevant to mass transport in sediments, namely, porosity, dispersivity, permeability and CEC. Next, the problems in applying the relationships to predict these parameters in the case of silt- and clay- rich sandstones are reviewed and extensions or new developments arising from this study are described.

A method for predicting porosity from the grain size distribution of a silt- and clay- rich sediment is developed, and is tested on different sets of data with widely varying properties. Various parameters of a grain size distribution of a sediment can also be used to predict the longitudinal dispersivity; this model is developed in the present study with extensive data from glacio- fluvial gravels. This present work also shows that the dispersivity of sandstones may be determined from knowledge of their formation factor, porosity and permeability. In the case of permeability the existing Carman- Kozeny equation is found to be applicable to these classes of porous media and to equivalent sandstones by using a concept of grain shape coefficients extended in this study to calculate the

specific surface of the sediment. This concept is shown to be pertinent also to the estimation of the CEC of a sediment from knowledge of the CEC of its component minerals.

2.2 Clay Mineralogy and Transport Properties

Clay minerals in the pore space of sands and sandstones, whether as detrital particles or authigenic mineral matter, may have a significant effect on local porosity, permeability and other transport properties of the rock. Effective porosity is reduced because of the physical filling of the pores and necks and the capillary pressure curve of the material is changed because of the redistribution of pore sizes. The large surface area to volume ratio of clay mineral pore-linings and fillings increases the hydraulic resistance of the pore channels and thus reduces the permeability.

The surface area of a clay is expressed as the *specific surface*, which is the surface area of the voids per unit mass or per unit bulk volume of clay. The surface area is chemically active and consequently adsorption and ion-exchange reactions occur, which affect the transport properties of the sediment. Table 4 shows the specific surface of various common clay minerals. Note that the effect of reduced particle size is to increase the specific surface considerably.

Implicit in studies of the porosity and permeability of natural sands is the understanding that the amount and

TABLE 4. SPECIFIC SURFACE AREAS OF CLAYS AND OTHER MINERALS

a) Generalised Relationships

Mineral	Specific	Surface
	cm^2/cm^3	cm^2/g
smectite	34.9E4	82E4
illite	39.6E4	113E4
chlorite	14E4	42E4
kaolinite	8.8E4	23E4
quartz	0.056†	0.15†
calcite		0.094E4†
gypsum		0.075E4†

b) Effects of Particle Size

Material	Composition	Size	Specific Surface* cm^2/g
quartz	-	99.8% < 44 mesh 87% > 200 mesh angular particles	0.019E4**
Clay A	Coarse kaolinite and mica	92% < 10 μm 80% > 2 μm	5.1E4
Clay B	mainly kaolinite	87% < 10 μm 59% > 2 μm	11.1E4
Clay C	South Devon ball-clay	79% < 10 μm 40% > 2 μm	24.9E4
Clay D	Pure, well-crystallised kaolinite	91% < 2 μm 72% < 0.5 μm	38.3E4

†varies with grain size

* assumes particles are discs with aspect ratio of 12.5

** assumes spherical particles

(Table 4a after Almon and Davies, 1981)

(Table 4b after Haynes, 1961; †after Van Olphen and Fripat, 1979)

nature of the clay-sized particles is important in estimating permeability from textural characteristics. This

fact was recognised by Fancher and Lewis (1933) as a possible factor in their experimentally determined relationship between permeability and mean grain size for nominally clean, well-sorted sands. Also the work of Denson et al. (1968), and Denson and Wu (1971) indicated the effects of montmorillonite and kaolinite, respectively, on the hydraulic conductivity of sand. They observed that the hydraulic conductivity of a sand with uniformity coefficient of 1.9, d_{50} of 0.03cm and d_{10} of 0.015cm was reduced practically to zero by addition of 2.5% by weight of montmorillonite; however, some 16% by weight of kaolinite was required to achieve the same effect.

Neasham (1977) describes the effects of discrete particle fills, pore-linings and pore-bridging clays on the petrophysical properties of fourteen fine to very fine-grained, well-sorted sandstones of varying clay content and morphology. His findings are summarized in Table 5. An example of the utility of Neasham's classification of authigenic clays is provided by Morris and Shepherd (1982), who studied the Bridport Sands of Dorset, England. These sands are fine grained lithic arenites which contain kaolinite, illite and mixed-layer clays as their main clay mineral suite. The considerable reduction of up to 20% and 80% of the air permeability of these sands to kerosene and water respectively is attributable to the swelling of pore-lining illite-smectite, and to the blockage of pore throats by dislodged kaolinite fillings.

The effect of the mineralogy of the authigenic clay on porosity and permeability is discussed also by Stalder (1973) and Rossel (1982) for Rotliegend sandstones from the North Sea. The large reduction in permeability for similar porosity between kaolinite and illite bearing Rotliegend sandstones is explained by contrasts in the crystallographic habit, specific surface area and mode of occurrence of these minerals.

These experimentally determined relationships between the clay mineralogy and transport properties must be incorporated into conceptual models of the sediment as a porous medium before they can be used as input to equations such as (1). Some approaches to this problem are discussed in the remainder of this chapter.

2.3 Fundamental Relationships

Bear (1972) describes a porous medium as an interacting, continuous, solid phase (the solid matrix of the sediment) and a discontinuous void space which is occupied by one or more fluid phases. For any porous medium it is possible to define a *Representative Elementary Volume* (REV), which is a statistically representative sample of the solid phase and a void space. The fundamental fluid flux balance equations of mass, momentum and kinetic energy are formulated on the microscopic scale within a continuum made up of both the solid matrix and the fluid phases, (Whittaker, 1966; 1969). However because the point values of

TABLE 5. EFFECT OF CLAY MORPHOLOGY ON PETROPHYSICAL PROPERTIES OF SANDSTONES

a) Generalised Relationships

Type of Clay Filling	Porosity and Air Permeability	Pore Size Distribution
Discrete Particle Clay	highest porosity and permeability	strongly related to (gsd); reduces median pore diameter
Pore-lining	intermediate porosity and permeability	minimal relation to (gsd); reduced pore sizes; poorly sorted
Pore-bridging	very low porosity and permeability	minimal relation to (gsd); very small and poorly sorted pore sizes

b) Petrophysical Data on Sandstones of Table 5a.

Sandstone	Porosity	Permeability (md)	Qv meq/l (meq/100g)*	% of Clay
(Discrete Particle Clay)				
Berea	.212	796	0.03(0.305)	5
Miocene S.	.229	1173	0.03(0.336)	5
Paluxy	.248	1037	0.02(0.249)	5
Cotton Valley	.141	150	0.06(0.372)	6
Tar Springs	.190	420	0.03(0.266)	3
(Pore-lining Clay)				
Tuscaloosa	.257	41	0.11(1.409)	15
Vicksburg	.183	7	0.14(1.161)	11
Houston	.109	0.82	0.13(0.589)	7
Wilcox	.132	1.4	0.37(2.084)	10
Frio	.265	58	0.36(4.807)	12
(Pore-bridging Clay)				
Vicksburg	.191	0.09	0.15(1.312)	20
Houston	.085	0.15	0.20(0.688)	10
Wilcox1	.111	0.31	0.54(2.497)	10
Wilcox2	.129	0.21	0.36(1.975)	10

Source: Neasham (1977)

* CEC computed using (44); bracketed values are in meq/100g.

parameters within a phase cannot actually be measured, it is impossible to describe the domain or work at this scale.

Averaging the point values over the REV allows passage from the microscopic level to a macroscopic level at which physical measurements are possible, (Slattery, 1967, 1969; Bear, 1972). Using this approach the conceptual model of the porous medium is translated into the constitutive equations which describe its hydraulic and transport properties. This translation usually requires the inclusion of one or more empirical coefficients in the constitutive equation to express the interrelationships between the solid matrix and the fluid phases. As Bear (1972) points out, the constitutive coefficients must be measured experimentally and cannot be derived from a theoretical analysis alone. It follows that parameters and coefficients measured on any given class of porous media can be applied globally to samples from that class of materials in order to predict the averaged property of interest. In order to preserve the dimensional similitude between the physical phenomena at the microscopic and macroscopic levels it is necessary to express the constitutive coefficients as tensor quantities.

Dullien (1979) shows that the three most important macroscopic structural parameters of a porous medium are its porosity, specific surface and permeability. Dispersion and adsorption of a solute in the pore space are controlled by the interaction of these parameters with the fluid flux. The domain of definition of all these parameters is that of the

REV comprising the ensemble of grains and pores within a core or grab-sample of a clastic sand or sandstone.

Various experimental techniques have been used to describe the REV within the network of voids in a porous medium. Attempts have been made to classify porous rocks on the basis of the gradient of the capillary drainage curve, (Thomeer, 1960; Robinson, 1966; Wardlaw and Taylor, 1976). Better characterisation has been obtained by impregnating the sample with resin (Wardlaw and Cassan, 1979) or Wood's metal (Dullien and Mehta, 1971/2) and then forming pore casts by dissolving the rock matrix. Stereologic techniques can then be used to analyse the geometry of pores and throats seen in thin sections and SEM photomicrographs of the etched pore casts, (Dullien and Dhawan, 1974). In general, the shapes may be visualised as spheroidal or irregularly shaped pore-chambers connected by narrow necks or throats. Figure 1, plotted from the data of Wardlaw and Cassan (1979) shows the relationship between the size of grains, throats and pores in a variety of sandstones of Jurassic and Cretaceous age. The throats are found to be sheet-like in shape and are seen on the Figure to be proportional to mean grain size.

The physical network of pores can be modelled by electrical resistance analogs with varying degrees of interconnectedness, (Fatt, 1956a,b,c; Schopper, 1966, 1967a,b; Chatzis and Dullien, 1977). However, because of topological constraints it is not possible to represent a

three-dimensional structure with a two-dimensional network.

Conceptual and mathematical models of the pore network have usually taken the form of bundles of cylindrical capillary tubes which are modified by various combinations of variable diameter and orientation to simulate different hydraulic and transport characteristics of the porous medium. A *tortuosity* concept, originally formulated by Carman (1937) as the square of the ratio of the actual flow path length to the shortest distance along the macroscopic flow direction, and shown to be a second rank tensor by Bear and Bachmat (1967), is used to account for the tortuous or irregular nature of the interconnected void space. Mathematically, the tortuosity is expressed as

$$\tau = (L_e/L)^2$$

where L_e is the actual flow path length and L is the shortest distance along the macroscopic flow direction.

2.4 Models for Estimating Porosity

In clastic sediments the porosity is a function of particle shape, size distribution and mode of packing, whereas in consolidated sandstones it is controlled primarily by the mineralogy of the cement and its spatial distribution within the pore space. One of the first approaches to establishing predictive models of porosity involved the concept of regular or irregular packings of uniform spheres. Graton and Frazer (1935) demonstrated the variation in porosity with the packing geometry of regular

arrays of uniform spheres.

Irregular or random packings of uniform and size-distributed spheres are described primarily by the *coördination number*, i.e. the number of spheres in contact with any specified sphere, and the *packing density*, $(1 - n)$, (Norman, 1971). Two types of random packings are recognised: dense and loose. In the former, the coördination number achieves a maximum value, as each sphere is tangent to all of its nearest neighbours; in the latter, gaps may exist between some of the spheres. Boerdijk (1952) and Wise (1952) used these principles to describe the packing density of such systems. Later workers used their findings in attempts to simulate the packing of spheres, (Norman and Maust, 1971; Norman et al., 1971; Visscher and Bolsterli, 1972; Tory et al., 1973). However, the application of such work to modelling the porosity of clastic sediments has been limited. The major impediment appears to be including the effect of particle shape on the packing density. Herdan (1960) reviews the derivation of geometric shape factors of particles and their estimation from grain size distributions.

The effects of a size distribution in spheres are twofold: there may be an increase in porosity due to bridging of particles, or there may be a decrease in porosity because of the infilling of void spaces by smaller spheres, (White and Walton, 1937). The development of bridging in packs of non-spherical, size-distributed

grains appears to be related to the angularity of the particles. An empirical relationship relating the volume of voids to ratio of smallest to largest size and to number of component sizes for a packing in which the smaller particles pack between the larger ones, was developed by Furnas (1929, 1931). Furnas (1929) found it useful to account for the angularity of particles by means of an "equivalent spherical diameter", defined as the diameter of a sphere of volume equal to the mean volume of a particle. An important result of these experiments is a series of graphs relating the voidage to the ratio of the smallest to the largest particle size for differing initial void volumes of each component. Later studies by Clark (1960) and Morrow et al. (1969) verified the general applicability of Furnas' work to artificial and natural mixtures of sand and silt.

The relationship of packing density to size range of component particles was examined by Sohn and Moreland (1968). They showed that packing density was a function only of the dimensionless standard deviation of grain size distribution and of particle shape; it was independent of grain size. Haughey and Beveridge (1969) review much of this work in the course of providing an overview of the packing properties of artificial and natural packs of particles.

The mode of packing of clastic sediments appears to be the primary control on the porosity of such media. Morrow (1971) developed the concept of packing heterogeneities as an index of pore structure, and indicated that packing

heterogeneities correlate with depositional environment and changes due to post-depositional diagenesis. Allen (1969) suggested that prolate spheroids would be a better model for packings of natural sand grains than spheres. He illustrated his ideas with sketches of thin sections of Devonian sandstones to demonstrate that similar packing densities could be attained with differing combinations of spheroidal axial-ratio and regular array. This lack of uniqueness might explain the variability observed by Gaither (1953) and Kahn (1956a,b) in their studies of coordination, packing and porosity of artificial and natural sands. Also, the initial packing of natural sands may be dense or loose, depending on the environment of deposition, (Pryor, 1972; Beard and Weyl, 1973).

Thus, theoretical sphere-pack models are useful surrogates only for clean, well-sorted, well-rounded and relatively homogeneous clastic sands. For the most part, however, clastic sands and silts consist of angular particles of quartz and other resistate minerals of differing bulk density forming locally heterogeneous random packings. The shapes of the particles of different minerals differ because of varying cleavage and fracture characteristics, so that the shape factors which may be applied to spheres are correspondingly variable. The presence of varying amounts of detrital clay and silt laminae further complicate the prediction of the mean porosity of a sample using a sphere pack model.

In view of the operational difficulties associated with sphere pack models, I have developed an empirical approach to predicting porosity from a grain size distribution by postulating a relationship between porosity and known controlling variables. From the work of Sohn and Moreland (1968) and Furnas (1929, 1931), possible predictor variables are the *uniformity coefficient*, (d_{60}/d_{10}) of the grain size distribution, and the ratio of the sizes of the largest component particle to that of the smallest. Also, the experiments of Morrow et al. (1969) indicated that the relative amount of silt-sized and smaller material in the sample is important. Selection of these parameters is in accord with knowledge of the structure of heterodisperse grain packs and they incorporate physically meaningful shape and packing variables.

Accordingly, it is assumed that the variables are related through an intrinsically linear relationship, in which any non-linearity is included in the coefficients of the equation. The relationship takes the functional form of:

$$n = f(UC, RF, RFF)$$

where

n = porosity, fraction

UC = uniformity coefficient

RF = weight of sample < 0.04mm/total weight of sample

(i.e. proportion of silt- and clay- sized particles)

RFF = ratio of largest to smallest particle size.

The operational definition of RFF is the ratio of the geometric mean aperture size of the pair of sieves defining the coarsest fraction to that of the finest fraction. Data listed in Appendix Table A1.3.1 were used to fit an equation to the functional relationship with a multiple regression program modified from Mather (1976). The equation is

$$n = .3516 - .09571(UC) + .2025(RF) + .3102E-4(RFF) \quad (2)$$

The value of $R^2 = .64$ and the fit is significant. The variables UC and RF are each strongly correlated with porosity, showing a correlation coefficient of .77 and .84 respectively; however, the correlation coefficient between RFF and porosity is .48. This low correlation is due probably to "noise" in the data, stemming from errors of estimation, as the smallest particle size is determined from extrapolation of the grain size distribution curve to the 99.99% of the distribution plotted on log-probability paper. Figure 2 shows the match between measured and predicted porosity.

The relationship in (2) may be applied to the estimation of the porosity of a disaggregated cemented sandstone by including the authigenic mineral matter in the fines for the RF term. However, the likely occurrence of authigenic mineral cement in the pore throats means that this estimate would probably be greater than the true effective porosity. In general, theoretical or empirical particle packing models of porosity are not applicable to clastic sandstones because the development of authigenic

mineral cements masks the effect of grain size and shape of the original sediment. Hence a more accurate estimate would be obtained from measurement on a thin section of the rock.

It is necessary to make a further correction to relate the thin section porosity to that measured on a plug of the material because of the nature of the pore space in sandstones which contain authigenic pore-linings and pore fillings. Pérez - Rosales (1976, 1982) proposed that for the conduction of electrical current the porosity of a saturated porous rock is twofold: there is a portion of the pore space through which the current flows, (flowing porosity), and stagnant zones in which there is no flow, (stagnant porosity). These stagnant zones correspond broadly to the 'dead - end' pores described by Deans (1963) and Coats and Smith (1964) in their studies of dispersion in sandstones. The flowing porosity is equivalent to the porosity observed with the optical microscope in thin sections of rock, (macroporosity, n_{mm}); the stagnant porosity is represented by the sub-microscopic porosity, n_m . With the aid of these definitions, the porosity may be restated as

$$n_{mm} = n_1^x \quad (3)$$

(Pérez - Rosales, 1982)

where

$$n_1 = \text{total porosity} = n_{mm} + n_m = n$$

x = a constant.

Iwuagwu and Lerbekmo (1981) show that core porosity measurements on clay rich sandstones by the "summation" of

fluids" method, (Monicard, 1980), yields n , because water adsorbed on the authigenic clays is included in the fluid balance. A plot of n_{mm} against n , Figure 3, measured on Belly River Sandstones conforms to the general relationship expressed by (3).

The method presented herein enables the estimation of the flowing (or effective) porosity of a clay - rich sandstone from laboratory measurements on core samples. Values of the constant x range from 1 in a system of dispersed spheres to 2, with a value of 1.73 being the average for sandstones, (Pérez - Rosales, 1982).

2.5 Models for Estimating Permeability

2.5.1 Constitutive Equations for Permeability

Hubbert (1956) demonstrated the physical basis of Darcy's empirical law of fluid flow in a porous granular medium. This derivation has been outlined subsequently in standard texts on groundwater hydrology, for example De Wiest (1965), Domenico (1972) and Freeze and Cherry (1979). Hubbert (1956) showed that Darcy's empirical permeability coefficient K in the equation

$$q = - K dh/dl \quad (4)$$

where

$$q = Q/A$$

$$Q = \text{volume flow rate} \quad [L^3/T]$$

$$A = \text{cross-sectional area of flow} \quad [L^2]$$

dh/dl = head gradient

could be expressed as

$$K = (Nd^3) (\rho/\mu)g \quad (5)$$

where

N = proportionality factor, dimensionless

d = mean grain diameter [L]

ρ = density of the fluid [M/L³]

μ = dynamic viscosity of the fluid [M/LT]

g = acceleration due to gravity [L/T²]

In (5) the Nd^3 term is a property of the geometry of the porous medium and defines the *intrinsic* or *specific permeability*, k , of the medium; k is a component of K , the *hydraulic conductivity* or *coefficient of permeability* of the porous medium. Hence

$$k = Nd^3 \quad [L^2] \quad (6)$$

$$K = k(\rho g/\mu) \quad [L/T] \quad (7)$$

(6) and (7) express the relationships for a homogeneous, isotropic porous medium, for example a uniform sand. Bear (1972) shows that both k and K are second rank, symmetrical tensors; hence, three mutually orthogonal principal directions can be assigned to components of these tensors.

Theoretical studies have attempted to relate k and K to parameters of the fluid and the medium with varying degrees of success. A general dimensional analysis is that presented by Rumpf and Gupte (1971) for single-phase, laminar flow in packs of spheres:

$$\Delta P/\rho v^2 = f\{vd/\nu, L/d, n, (gsd), \text{particle shape},$$

structure}

where

ΔP = pressure drop over distance, L

ρ , v , ν = fluid density, velocity & kinematic viscosity respectively

$\bar{d}$ = mean grain diameter

n = porosity

(gsd) = parameters of grain size distribution

Rumpf and Gupte (1971) found that for variously sorted sphere packs they could write:

$$f = C(5.6/Re)n^{-3.3}$$

where

f = friction factor for sphere pack

C = empirical constant (= 1, narrow size range; = 1.05, wide size range)

(in general, $C = f[\text{particle shape, (gsd) and structure}]$)

Re = Reynolds Number for the flow = $d\nu\rho/\mu$

μ = dynamic viscosity of the fluid

whence

$$k = d_2^3 n^{-3.3} / 5.6C \quad (8)$$

where

d_2 = surface average sphere diameter

(8) may be generalised to:

$$k = d_2^3 f(n) / f(C) \quad (9)$$

Because of the variation of these parameters in natural and artificial granular materials, many expressions for $f(n)$ and $f(C)$ have been derived, based on different concepts of the

geometry of the void space. Appropriate representations for (9) are based mainly on studies of the mechanics of flow in conduits as a model of flow in pores, (Dullien, 1979).

These conduit flow models are primarily empirical, phenomenologically based techniques which use laboratory or field studies of textural parameters of the porous medium and fluid mechanics principles to predict permeability. They are based on Darcy and Poiseuille laws for flow of a viscous fluid through a circular capillary, modified by suitable shape factors. A variant of these approaches is to relate the statistical properties of the grain size distribution to permeability, (Masch and Denny, 1966; Morrow et al., 1969; Beard and Weyl, 1973). Also, statistical models based on a fitting of pore sizes to empirical or theoretical size distributions have been proposed to relate porosity and permeability, (Childs and Collis-George, 1950; Marshall, 1958; Millington and Quirk, 1959, 1961). In the following sections conduit flow models will be examined in detail.

2.5.2 Phenomenological Flow Models

The early empirical, phenomenological models attempted to attach a functional value to the proportionality factor, N , and to determine some effective grain size parameter, d , in (5). Hazen in 1892 and Schlichter in 1899, cited in Loudon (1952), gave the following expressions for intrinsic permeability:

$$k = C(d_{10})^2 \text{ (Hazen); } k = (771d^2)/c \text{ (Schlichter)}$$

where

C = dimensionless parameter ≈ 100 ; range...41 - 146

d_{10} = grain size, mm., s.t. 10% of the material is of smaller size,

d = diameter of uniform sphere, (in)

c = $f(\text{porosity})$

The Hazen equation has been applied to alluvial material (Bedinger, 1961) and to fluvio-glacial sands and gravels (Norris and Fiddler, 1965). A similar equation was established by Wiebenga et al. (1970) from measurements on natural and artificial sand-sized material. Nevertheless, equations of this type are applicable mainly to well-sorted, well-rounded, clean sands with a uniformity coefficient of three or less, (Lyon, 1985). With continuing research, models incorporating a more diverse array of characteristic parameters were developed. For instance, Krumbein and Monk (1943) expressed k in dimensional terms as

$$k = f(d^2, \sigma_s, M, \sigma_s, H)$$

where

d^2 = average grain diameter squared

σ_s = standard deviation of grain size

M = mean shape (sphericity)

σ_s = standard deviation of shape

H = dimensionless packing parameter related to shape and orientation of the particles

By assuming that the particulate material followed a log-normal distribution of grain sizes, an equation relating

k to geometric mean diameter and statistical parameters of the observed distribution was derived.

Berg (1970) extended the analysis of Krumbein and Monk (1943) by considering the packing in terms of the regular array of spheres envisaged by Graton and Frazer (1935). Berg (1970) considered the shapes of the interparticle void spaces in the various arrays as analagous to geometric ducts for fluid flow. He then adapted analytical solutions for flow rate through ducts of similar shapes in order to relate k to grain size and porosity for various packings. By combining the effects of packing, grain size distribution, sorting and grain shape, Berg (1970) finally arrived at the relationship for k:

$$k = 5.1E-6n^3 \cdot (Md)^2 \exp(-1.385PD\phi) \text{ darcies} \quad (10)$$

where

n = porosity, percent

Md = median grain size, mm

PD ϕ = phi percentile deviation of grain size distribution

= (P₁₀ - P₉₀)/2 in phi units

P = percentile of grain size distribution

This relationship is applicable to well-sorted, granular porous media of 30% to 40% porosity. An equivalent geologic medium would be an unconsolidated, clean sand or friable sandstone with well-rounded grains, (Berg, 1970).

An equation which does not require assumptions about the form of the grain size distribution was derived by Fair

and Hatch (1933):

$$k = \{P'[(1 - n)^2/n^3][(S/100)\Sigma(P/d)]^2\}^{-1} \quad (11)$$

where

n = porosity

S = shape factor varying between 6 for spheres and 7.7 for angular sands

P = weight percentage of grains of a given diameter (from gsd)

d = geometric mean of adjacent screen sizes

P' = packing factor, usually ≈ 5

This equation is applicable under conditions similar to those described previously for that of Berg (1970).

A relationship which is equivalent to the Fair-Hatch equation but computationally is less cumbersome is the so called Carman - Kozeny equation. Carman (1937, 1938, 1939) modified the original relationship proposed by Kozeny in 1927 to the form commonly used at the present time:

$$k = n^3/cS_0^2(1 - n)^2 \quad (12)$$

where

$$c = c_0 r \approx 5$$

r = tortuosity

c_0 = factor relating pore cross-sectional shape to that of a circle; e.g.

$c_0 = 1.94$ (rectangle with length twice width);

$c_0 = 2.00$ (circle);

$c_0 = 2.13$ (ellipse with long axis twice short axis);

$c_0 = 3.00$ (infinite parallel slot);

S_0 = specific surface of particles $[L^2/L^3]$

The term cS_0 incorporates the effects of grain diameter and surface area exposed to the flow. Subsequent experimental work confirmed the importance of porosity and particle shape variations in (12), (Bakhmeteff and Feodoroff, 1937; Hatch, 1938, 1940; Rose 1945a, 1945b, 1949; Coulson, 1949).

The shape factors of each grain are related both to its dimension ratios and its irregularity of shape as compared to an equidimensional particle. Heywood (1947) derived formulas for computing the volume shape factor, α_0 , and the surface shape factor, α_s , in terms of the measured width-to-thickness and length-to-width ratios of angular, sub-angular and rounded particles of various geometric shapes. On the basis of numerous experiments by different investigators, the following typical ranges of values of the shape coefficient, α_s/α_0 , can be assigned to various shapes and minerals: *flakes*, 20 - 75; *irregular cuboids*, 10 - 16; *angular quartz*, 7 - 19; *spheres*, 6 ; (Herdan, 1960; Allen, 1968; Jelinek, 1970; Silverman et al., 1971; Stockham and Fochtman, 1977). The specific surface of the porous medium can be estimated from knowledge of the shape coefficients and sizes of its component particles.

In contrast to purely phenomenological approaches the Carman-Kozeny equation is based on the concept of the void space of a porous medium as a bundle of irregularly shaped capillary tubes with a constant averaged area, (Dullien, 1979). The hydraulic behaviour of this system may be

approximated to that of equivalent cylinders by weighting with a shape factor, and use of the tortuosity concept to account for the irregular fluid flow paths. The equivalent channel diameter is described in terms of the hydraulic radius, m , (Carman, 1939), defined as the ratio of the cross-sectional area of the conduit axis to the length of the perimeter of the conduit wetted by the fluid. For unconsolidated clastic sediments this definition becomes simply the ratio of porosity to the specific surface of the particles.

In practice the difficulty of accurately determining the hydraulic radius and tortuosity can be formidable. Microscopic roughness on the pore walls due to irregular grain shape or authigenic mineral growths can create significant errors in the estimation of the hydraulic radius. Nevertheless, in the absence of experimental measurements of surface area, acceptable estimates can be based on the abundances of particles of different shapes. The tortuosity can be stated in terms of the *formation factor*, F , because of the direct analogy between fluid flow and electrical conductivity of porous media.

The formation factor is defined as the ratio of electrical resistance of a saturated porous medium to the resistance of the saturant fluid, (Wyllie and Spangler, 1952), so that F can be shown to be related to porosity, n , by means of

$$F = an^{-x}, \text{ (Pfannkuch, 1972).}$$

Values of x approximate 2 and n is close to 1, (Von Gonten and Whiting, 1967), but Pérez-Rosales (1976) suggests 1.3 for packs of spheres; Winsauer et al. (1952) put $a = 0.62$ and $x = 2.15$, which is the commonly used empirical Humble formula for clean, cemented sandstones. Since tortuosity may be expressed as F_n or $(F_n)^2$, (Street, 1958), depending on whether the cross-section area for flow is defined as nA or nAL/L_e , where A is the actual cross-sectional area of the medium, the Carman-Kozeny equation may be modified to:

$$k = (m^2/c_0) F^{-x} n^{-1} \quad (13)$$

(Wyllie and Spangler, 1952; Hubbert, 1956; Stephens and Lin, 1978)

Brace (1977) suggests that for a wide range of rocks, (13) can be simplified to:

$$k = (m^2/c_0) F^{-1.3} \quad (14)$$

if the relationship of Archie (1942), namely $x = 2$ and $a = 1$, is assumed.

2.5.3 Estimation of Permeability

The limitations of sphere pack models of granular material for the prediction of permeability are similar to those for estimating porosity. The specific surface of the grains is a key factor in controlling permeability and it, in turn, is related to the shapes and mode of packing of the particles. Hence the sphere or spheroid pack is an adequate representation only of clean, well-sorted, well-rounded, homogeneous clastic sands. The convenient application of the

Fair- Hatch or Carman- Kőzeny equations to the calculation of permeability of silty or clayey sands depends on the ability to estimate the specific surface of such media. In these media the particle shape departs markedly from that of a sphere. However, a method for calculating the specific surface taken, with minor modifications, from Herdan (1960), is outlined below.

An expression for the surface area of a bed of solid, non-porous particles may be derived from a grain size distribution. Assuming that the particles are spheres, the surface area, S , and the volume, V , of each particle is

$$S = \pi d^2; V = (\pi/6)d^3$$

where

d = mean projected diameter of particle.

For a size distribution of particles in the bed, S and V of the bed become

$$S = \pi \sum d_i^2 N_i; V = (\pi/6) \sum d_i^3 N_i$$

where

d_i = mean projected diameter of particles in the i th size class

N_i = number of particles in the i th size class

Σ = summation from i to m classes.

Forming the ratio S/V yields the specific surface, S_v .

$$S_v = (6 \sum d_i^2 N_i) / \sum d_i^3 N_i = 6/d_v$$

where

d_v = reciprocal of the volume - surface diameter of the sphere.

Herdan (1960)

In the case of non - spherical particles the factor 6 has to be replaced by the ratio α_s/α_v of the surface and volume shape factors, α_s , and α_v . Where the size distribution of the particles is determined as a weight distribution from sieving, the surface area per unit mass, S_m , is used, i. e.

$$S_m = (\alpha_s/\alpha_v)(1/\rho d_s)$$

where

ρ = density of the particle.

Herdan (1960) shows that the expression for S_m then becomes

$$S_m = \alpha_s/\alpha_v \rho \sum (w_i/d_i) \quad (15)$$

where

w_i = weight of particles in sieve class i

d_i = mean size of particles in sieve class i .

(15) is applicable to particulate assemblages in which the particles are all of the same mineralogical composition. The equation may be modified to calculate the specific surface of grains which differ in shape and composition between classes. In this latter form it becomes

$$S_m = \sum \{[(\alpha_s/\alpha_v \rho)]_i (w_i/d_i)\}$$

$$S_o = \rho S_m \quad (16)$$

(16) can then be applied to calculate the specific surface term, S_o , in the Carman - Kozeny equation for determination of the permeability of sands with admixtures of silt and clay. The application of the technique to samples from Datasets 1 and 2 is fully described in Appendix 1. Figure 4 shows the match between the permeability predicted by this

method and that measured in the laboratory. The decrease in precision in low permeability materials is notable; this deviation is ascribed to the difficulty in estimating the shape factors of mixtures of silt and clay particles from the lithological description of a sample.

Because the average shape coefficients of a size fraction are related to the mineral composition of the fraction through the effective morphology of the minerals, it follows that the shape coefficients may be estimated from a detailed knowledge of the mineral composition. Thus, the shape coefficients of individual minerals are weighted by the proportional concentration of the mineral to compute the average shape coefficient for that size fraction or size class. In the absence of detailed measurements of the shape coefficients of mineral grains, recourse is made to the representation of minerals by the shape coefficients of idealized shapes.

The permeability of sandstones which are only slightly cemented such that the original grain size distribution remains the dominant microstructural element may be found from application of (12) without great loss of accuracy. However, for sandstones in which authigenic minerals occupy part of the pore space, either (13) or (14) is applicable. In these cases it is necessary to estimate the shape factor c_0 and the hydraulic radius, m , in (13) or (14). The shape factor is relatively insensitive to changes in pore shape, and an average value of 2.5 may be assumed, (Stephens and

Lin, 1978).

Starting with the definition by Carman (1939), the hydraulic radius of a pore which is coated by an authigenic mineral can be approximated by

$$m = n/[w\rho S_m(1 - n)] \quad (17)$$

where ρ and S_m refer to the mineral species, and w represents the proportional mass of the mineral. Assuming that the authigenic mineral is composed of equidimensional particles, the effective external surface area per unit volume of the coating is $x\rho S_m$, in which x is the ratio of the areal dimension of the face contacting the flowing fluid to the dimensions of the other faces. In the case of a cube, the expression becomes 0.175. This approximation is broadly representative of smectite and kaolinite booklets and sheets, (Brown et al., 1978); other geometric shapes such as prisms would be better representations, for example, of illite laths, and cylinders would more closely approximate tubular vermiculites. In general, a tractable, averaged approximation to the hydraulic geometry of a pore mineral particle would be a regular polyhedron with m faces, so that the ratio x can be approximated by $1/m$.

Roberson et al. (1968) have shown that Na-saturated montmorillonite tend to form roughly equant, platelike microaggregates. Realistic dimensions can be assigned to these shapes from the comprehensive measurements made by Wilson and Pittman (1977). Alternatively, estimates of S_m may be obtained from published experimental measurements.

The relationship expressed by (17) can be extended to include the influence of p mineral species forming a pore lining if it is rewritten as

$$m = n / \sum [w_i \rho_i S_{mi} (1 - n)] \quad (17a)$$

where the summation of i is from 1 to p .

The remaining term to be evaluated in (13) or (14) is the formation factor, F . Pérez - Rosales (1982) shows that F is related to tortuosity, τ , and porosity, n , by

$$\tau = n(Gn^x + 1 - G) \quad (18)$$

$$F = \tau/n$$

from which

$$F = Gn^x + 1 - G \quad (19)$$

where x is analogous to the exponent in (13) and G is a coefficient which is characteristic of the internal geometry of the porous medium. Table 6 gives typical values of G and x .

The relationships expressed by (14), (17) and (19) were applied to the prediction of permeability of samples of Belly River sandstones of Data Set 5. Table 7 displays the results, which were calculated using the porosity, mean grain size and mineral composition listed in Appendix 1. The specific surface of individual minerals is taken from published data and from Table 4 respectively. A plot of the experimentally determined relationship between the specific surface and permeability of various sandstones using data from Almon (1979) is presented in Figure 5.

TABLE 6. VALUES OF G AND x

Media	G	x
Spheres	1.49	1.09
Cubes	1.33	1.28
Sandstones	1.03	1.73

Source: Pérez- Rosales (1982)

TABLE 7. MEASURED vs PREDICTED PERMEABILITY, BELLY RIVER SANDSTONE

Sample	Permeability (millidarcies)	
	Measured*	Predicted
8	573	836
9	26	52
10	0.5	0.15
11	27	16
12	1.4	39
13	0.8	0.43
14	<0.1	0.28
15	193	70
16	0.3	0.34
17	680	560
18	100	36
19	12	42
20	31	20
21	117	82
22	75	36
23	164	149
24	80	19
25	4.5	5.7
26	29	2.5
27	26	1.5
28	<0.1	1.8
29	123	148
30	313	386

* Source: Iwuagwu and Lerbekmo (1981)

In this Figure the specific surface data other than that of Almon (1979) is obtained by the method described in this chapter. The values, except for some sandstones with

pore lining clays, fall within the weakly defined trend of Almon's experimental data. The departures from the trend likely are the result of incorrect assumptions about the mineralogy and morphology of the authigenic clays in those samples.

This analysis is strictly applicable only to sandstones in which the pore saturant is a single - phase conductive fluid, e.g. brine, so that the conductive - solid effect of the authigenic clay is minimised. Where the resistivity of the saturant fluid is high, as is the case in freshwater - aquifers, the presence of the conductive clay coating on the rock matrix acts to reduce the value of F , (Patnode and Wyllie, 1950), and (14) is no longer applicable. Methods for correcting F to obtain the true formation factor have been described by Hill and Millburn (1956), Worthington and Barker (1972) and Worthington (1977).

2.6 Models of Dispersivity

2.6.1 Constitutive Equations for Dispersivity

Dispersivity is a property of the porous medium which affects the spread or dispersion of solutes being transported in the fluid flowing through the medium, (Freeze and Cherry, 1979). The actual dispersion of a solute is caused by the variations in flow velocity in the pore channels along the direction of average flow, (*mechanical dispersion*; Bear, 1979), in conjunction with the variations

in solute concentration created by Fickian diffusion along a solute concentration gradient, (*molecular diffusion*; Bear, 1979). The *coefficient of hydrodynamic dispersion*, D , is the sum of these factors and is expressed as

$$D = \alpha \tilde{v} + D_0 \quad (20)$$

where

α = dispersivity [L]

$\tilde{v}$ = average velocity [LT⁻¹]

D_0 = coefficient of molecular diffusion for the solute [L²T⁻¹]

Conceptualisation of the dispersivity of a porous medium can be accomplished by the spatial averaging technique developed by Bear and his co-workers, (Bachmat and Bear, 1964; Bear and Bachmat, 1967; Bear, 1969, 1972). In this approach the averaged fluid transport equations are derived by averaging over the REV and the dispersion coefficient in a model of interconnected capillary tubes is a second rank, symmetric tensor, (Bear and Bachmat, 1967):

$$D_{ij} = a_{ijkl}(\tilde{v}_k \tilde{v}_m) / \tilde{v} \cdot f(\text{Pe}, \delta) \quad (21)$$

where

D_{ij} = coefficient of hydrodynamic dispersion

$\tilde{v} = |\tilde{v}|$ = average fluid velocity given by:

$$\tilde{v} = q/n$$

Pe = Peclet Number = $L\tilde{v}/D_0$

$\delta = R/L$ (ratio of averaged channel hydraulic radius to characteristic length of pores)

$f(\text{Pe}, \delta)$ = mass transfer by molecular diffusion between

adjacent streamlines

(usually takes the form, $Pe/(2 + Pe + 4\delta^2) \approx 1$ for most cases)

The coefficient a_{ijkl} is a fourth rank symmetric tensor, (Scheidegger, 1961), and is a fundamental geometric property of the porous medium. Bear and Bachmat (1967) and Bear (1972) express this quantity as:

$$a_{ijkl} = [(B_{ik}Br_{jl})' / (Br_{km})' \cdot (Br_{ln})'] L \quad (22)$$

where

B = hydraulic conductance of channel at the point being averaged

r_{ij} = tortuosity of the medium

L = characteristic length

and the prime (') indicates spatially averaged quantities. They showed that a_{ijkl} was related to components of α parallel and normal to the mean flow direction respectively, namely the *longitudinal dispersivity*, α_1 , and the *transverse dispersivity*, α_2 . Using these parameters they could write:

$$a_{ijkl} = \alpha_2 \delta_{ij} \delta_{km} + (\alpha_1 - \alpha_2) / 2 \cdot (\delta_{ik} \delta_{jm} + \delta_{im} \delta_{jk}) \quad (23)$$

where

δ_{ik} = Kronecker delta

Hence combining (21) and (23):

$$D_{ij} = \alpha_2 \tilde{v} \delta_{ij} + (\alpha_1 - \alpha_2) \cdot (\tilde{v}_i \tilde{v}_j) / \tilde{v} \quad (24)$$

If D_{ij} is written in Cartesian coördinates such that one of the axes is parallel with the direction of $\tilde{v}$, then D_{ij} can be put in the form of a matrix:

$$\begin{bmatrix} \alpha_1 \tilde{v} & 0 & 0 \\ 0 & \alpha_2 \tilde{v} & 0 \\ 0 & 0 & \alpha_2 \tilde{v} \end{bmatrix} = [D_{ij}] \quad (25)$$

For homogeneous, isotropic media Bear (1972) demonstrated that the matrix could be simplified to:

$$D_{11} = \alpha_1 U$$

and

$$D_{22} = \alpha_2 U$$

in which the symbol U replaces $\tilde{v}$ for convenience. As a result of the foregoing, the final form of (20) is:

$$D_{11} = \alpha_1 U + D_0 \quad (26)$$

$$D_{22} = \alpha_2 U + D_0 \quad (27)$$

where D_{11} and D_{22} are, respectively, the *longitudinal* and *transverse* dispersion coefficients. In general, laboratory measurements show D_{22} to be approximately an order of magnitude less than D_{11} , (Crane and Gardner, 1961; Perkins and Johnston, 1963).

Studies of dispersion at the microscopic level have often been based on the analysis of flow and solute transport in a single capillary tube. The classical work of Taylor (1953, 1954) and Aris (1956) discussed the fundamental concepts of dispersion in capillary tubes. Refinements on the Taylor-Aris model of dispersion include the studies by Turner (1958) and Aris (1959a, 1959b) to incorporate dead-end pores, and the work of Dayan and Levenspiel (1968) who showed that the effect of adsorption

was to modify the value of the dispersion coefficient in a capillary tube, D_c . Various other workers have examined the effects of variation from the ideal cylindrical capillary tube and numerous expressions for D_c have been published. Dullien (1979) reviews much of this work, which refers to flow in tubes and through ducts of known geometry and dimensions.

Fried and Combarous (1971) and Fried (1975) argue that dispersion in a capillary tube is not comparable to flow in a porous medium: in the former case it is due to variations in the velocity profile within the tube, whereas in the latter, dispersion results mainly from the velocity variations in the streamtubes imposed by the tortuosity of the medium. Also, there is dispersion which is induced by mixing at the junctions of capillaries within the porous medium. In addition, D_0 must be replaced by D^* , the *effective coefficient of molecular diffusion* in porous media. D^* is D_0 modified by a factor that is a function of the porosity for non-reactive tracers in chemically inert media, (Mackie and Meares, 1955; Prager, 1960; Domenico, 1977). In spite of these considerations, conceptual models of porous media as bundles of capillary tubes of an overall random or directed orientation, with variable pore length, radius and degree of interconnection, can be used to describe dispersion in clastic sands and sandstones.

Saffman (1959a,b; 1960), and de Josselin de Jong (1958) independently used a random walk approach to the estimation

of dispersion in an ensemble of randomly oriented, uniform, cylindrical, straight capillary tubes. Haring and Greenkorn (1970) extended Saffman's work to include the effects of non-uniform pores. Starting with the pore network of Saffman they included variability in the radius, length and orientation of capillaries.

The Turner model and its derivatives was used as the basis of later work by Deans (1963), Coats and Smith (1964), Passioura (1971), De Smedt and Wierenga (1979a, 1979b) and van Genuchten (1985) on dispersion in porous media which contain micropores. In practice it is difficult to obtain accurate measurements of the geometry of capillary tubes and pore networks, and it is usual to infer D_{11} and D_{22} from statistical correlations between groups of parameters characteristic both of the fluid and the porous medium. For example, Harleman et al. (1963) plotted the following sets of parameters measured on glass beads and well-sorted, clean sands:

$$D_{11}'/\nu \text{ vs. } R(d_{50}) \text{ and } D_{22}'/\nu \text{ vs. } R(k)$$

where $R(d_{50})$, $R(k)$ are, respectively, the Reynolds Number for d_{50} of a grain size distribution, and for intrinsic permeability; D_{11}' and D_{22}' are respectively, the dispersion coefficient longitudinal and transverse to the flow direction. They found that for packs of spherical beads and sand, both rounded and angular, but with a range in uniformity coefficient of 1 to 1.15, the following correlations were valid:

$$(D_{11}/\nu) = c_1 R(d_{s0}) = c_2 R(k)^m$$

$$(D_{22}/\nu) = c_3 R(d_{s0}) = c_4 R(k)^m$$

where

$$c_1 = 0.66; c_2 = 54; c_3 = 0.9; c_4 = 88; m = 1.2$$

Harleman et al. (1963) suggest that m is a function of grain size distribution and tends towards 1 as the medium becomes less uniform. The form of the relationship is similar to that determined by Ebach and White (1958) for dispersion in columns packed with variously shaped particles. These statistical correlations show that the relationship is dependent largely on grain size and fluid velocity; particle shape appears to have negligible effects.

Fried and Combarous (1971) have used dimensional analysis to determine the variables which control dispersion in porous media. They state that

$$\text{Dispersion} = f\{D^*/D_0, (U/k)/D^*, \mu_1/\mu_2, (g\Delta\rho k^{3/2}/\mu D^*)\}$$

where

μ_1, μ_2 = viscosity of solute and solvent, respectively, before they mix.

Of these four dimensionless groups, D^*/D_0 represents the effect of molecular diffusion and has been shown to be represented as $1/Fn$, (Perkins and Johnston, 1963). $(U/k)/D^*$ is the Peclet Number, which expresses the interaction between the texture of the rock and the velocity of the fluid. The two remaining groups represent respectively the viscosity and density contrast between the solute and solvent. They can be neglected for the tracer case of

dispersion.

Mostly these fundamental ideas of dispersion have been developed from theoretical considerations and laboratory scale measurements. However there can be problems in applying these concepts to field situations. For instance, Gillham et al. (1984) point out that in some types of heterogeneous geologic media, for instance alternating layers of shale and sandstone, solute transfer by molecular diffusion from the shales to the sands may be an important component of the dispersion mechanism under the normal range of flow velocities. Another problem with the estimation of α_1 and α_2 is that these parameters appear to be scale-dependent. Differences of several orders of magnitude for values of α_1 and α_2 between laboratory columns and cores and those from field tracer tests suggest that these parameters are related to the volume of the porous domain being tested, (Anderson, 1979; Pickens and Grisak, 1981; Gillham and Cherry, 1982).

Attempts to explain the variation in magnitude of α_1 and α_2 with the scale of the flow system being studied have focussed on two main areas, viz.

- (a) definition of the process on the micro-, macro-, and mega-scales of heterogeneity, and of the effects of heterogeneity within the flow field; (Skibitzke and Robinson, 1963; Mercado, 1967; Greenkorn and Kessler, 1969; Bear, 1972, 1977; Schwartz, 1977; Smith and Schwartz, 1980, 1981; Silliman, 1981; Gillham and

Cherry, 1982 ; Gelhar and Axness, 1981, 1983).

(b) the dimensionality of the flow domain; (Domenico and Robbins, 1984; Robbins and Domenico, 1985).

The micro- and macro-scales are related to the the previously defined REV concept and for transport parameters may be considered to be respectively the individual pore channel or flow tube and the ensemble of grains and pores making up a network of flow channels. Dispersion can be modelled on both of these scales, but the values are of little practical significance except in uniform, homogeneous media. In natural sediments the significant textural variations on the scale of separate laminations a few centimetres thick engender large variations in the velocity components of flow and it is impractical to measure the resulting variation in the dispersion coefficients. Hence recourse must be made to the megascopic scale defined by Bear (1977). This technique represents a mathematical averaging over the entire thickness of the layers encompassed by the flow domain, and a *coefficient of macrodispersivity*, (Bear, 1979) is obtained, which is analogous to the local dispersion coefficients.

2.6.2 The Estimation of Dispersivity

Numerous experimental observations indicate that the dispersion of a tracer in a uniform, homodisperse or single-size sand column is controlled by the velocity of the fluid and the grain size of the sand. For heterodisperse

sand both the mean grain size, d_{50} , and the spread of the grain sizes, expressed by the uniformity coefficient are important. In the case of silty sands with detrital clay minerals both the velocity - induced mixing in the macropores and molecular diffusion in the micropores within the detrital clays may be significant. Similar considerations apply to sandstones with authigenic pore minerals.

From the dimensional analysis of Fried and Combarous (1971) it is clear that plots of Peclet Number against the ratio of longitudinal dispersion to molecular diffusion would incorporate all the significant variables which control dispersion. Values of Peclet Number, fluid velocity and D_{11}/D_0 have been computed from data published by various investigators who used packs of single sized, artificial or natural particles and sandstone cores, (Carberry and Bretton, 1958; de Josselin de Jong, 1958; Blackwell, 1962). Some measurements by Brigham et al. (1961) and Martin (1971) of longitudinal dispersion on sandstones are tabulated in Appendix 2. List and Brooks (1967) have summarized the data from similar work on transverse dispersion. On the scale of the laboratory column, dispersion in homodisperse granular materials follows well - defined trends within different ranges of the Peclet Number. For values of $Pe < 1$ the plot of D_{11}/D_0 against Peclet Number is flat and tends towards

$$D_{11}/D_0 = 0.67 \quad (\text{Fried and Combarous, 1971})$$

and

$$D_{22}/D_0 = 0.7 \quad (\text{ibid.})$$

so that molecular diffusion is the most important mechanism of dispersion. For Pe between 0.4 and 5 there is a transition zone to the régime of mechanical dispersion, with an upper limit of $Pe \approx 1E5$ for laminar flow, (Bear, 1979). Since the log-log plots are linear, a power law relationship is postulated, of the form

$$D_{11}/D_0 = D^*/D_0 + \alpha(Ud_m/D_0)^m, \quad 5 \leq Pe \leq 100 \pm \quad (28)$$

where d_m is the mean grain diameter and where, for D_{11} ,

$$\alpha \approx 0.5 \quad \text{and} \quad m \approx 1.2$$

and, for D_{22} ,

$$\alpha \approx 0.025 \quad \text{and} \quad m \approx 1.1$$

At higher ranges of Pe , the effects of molecular diffusion are negligible, so that the slope becomes 45° and $m \rightarrow 1$; (28) is then reduced to

$$D_{11}/D_0 = \beta Pe \quad \beta \approx 1.8 \quad (29)$$

The effects of a distribution of grain sizes on dispersion in sand and gravel was examined using data abstracted from graphs presented by Klotz et al. (1980). These data are tabulated in Appendix 2 and plotted on Figures 6 and 7. The departures from the trend line of (28) and (29) are illustrated clearly by Figure 6 and are related to the sorting of the sands as described by the uniformity coefficient.

Inspection of the plot in conjunction with uniformity coefficient and d_{10} data indicates that these variables control the deviation from the trend line. The actual values

of UC and $d_{s,0}$ are listed in Appendix Table A2.1.1. Increases in the magnitude of both UC and $d_{s,0}$ result in, respectively, larger and smaller values of dispersivity. The effect is illustrated by sample sets 6 through 10 which show the influence of increasing UC from 1.1 to 20 at a constant $d_{s,0}$ of 0.1 cm. On the other hand, increasing the $d_{s,0}$ from .27 cm. to .63 cm. in sample sets 4 and 5, at a constant UC of 1.3 resulted in a decrease in dispersivity of similar magnitude, whereas sample sets 11, 12 and 13 show dispersivities which are relatively insensitive to a range in UC of 1.13 to 18.8 and an accompanying range in $d_{s,0}$ of .035 to .01 cm.

Klotz et al. (1980) fitted a relation of the form

$$D_{1,1} = BU_m^m \quad (30)$$

where B and m are constants and U_m is the flow velocity of the groundwater between two points on the same flowline. B has the dimensions of length as long as $m = 1$. In this case B is equivalent to the dispersivity, α_1 . Figure 7 graphs the relationship between B and, respectively, $d_{s,0}$ and UC. The plots show a trend of an increase in B with increasing $d_{s,0}$ and UC; the trend is more clearly marked for UC and confirms the greater effect of this variable on dispersivity as suggested by the various sample sets of Figure 6.

Klotz et al. (1980) identify the components of B as $f(UC, d_{s,0})$. Accordingly, on the basis of their data an equation

$$B = a(UC)^v d_{s,0}^z$$

was fitted, using a multiple linear regression program modified from Mather (1976). For these data, B is given by

$$B = 0.026(UC)^{-0.5} d_{50}^{-0.5} \quad (31)$$

The coefficient of multiple correlation, R^2 is 0.76. It is possible that more of the variance could be explained if d_{50} were included as a variable, but it was not reported for a sufficient number of samples. Variations in d_{50} should, in theory, affect the mean pore length and hence the Peclet Number for the flow. (30) and (31) provide a means of estimating D_{11} of clastic sands over a range of Pe values typical of groundwater flow velocities encountered in practice. For these values of Pe, (28) may be modified to

$$D_{11}/D_0 = D^*/D_0 + B(U/D_0)^m \quad (32)$$

Measurements of D_{11}/D_0 on sandstone cores are plotted on Figure 8, and are seen to yield values comparable to those determined on less well - sorted sands. This increase in the value of D_{11} is explained by Dullien (1979) as being related to the greater number of both serial and parallel pore non - uniformities in clastic sandstones compared to well - sorted sands or homodisperse sphere packs. The velocity differences between the large and small parallel non - uniformities and the pore necks and pore chambers of the serial non - uniformities account for the increased dispersion due to mechanical mixing.

The parallel trend of the experimental data for unconsolidated media and sandstones shown on Figures 6 and 8 suggest that the relationship to Pe follows a similar

mathematical form for both classes of porous media. Thus, Fried and Combarous (1971) cite expressions in which the grain size parameter of (28) is replaced by a term (ηd) in which η is a dimensionless constant that varies with the standard deviation of the velocity distribution, and d is a measure of grain size. A typical equation is that of Legatski and Katz (1967), which takes the form

$$D_{11}/D_0 = 1/Fn + 0.5(Ud\sigma/D_0)^m$$

where

$d\sigma$ = a characteristic length of the porous medium

σ = a packing factor.

These investigators measured $d\sigma$ for sandstones and dolomites with a range of permeability from 4.45 millidarcies to 1030 millidarcies; porosity and formation factors were also measured on the samples. The assumed functional relationship is

$$d\sigma = f(\sqrt{k}, n, F)$$

and the equation

$$d\sigma = -.0241 - .00219(\sqrt{k}) - .1071n + .0435F \quad (33)$$

fits the data of Legatski and Katz (1967) with $R^2 = .52$, where k is expressed in millidarcies. An estimate can thus be made of $d\sigma$ from a knowledge of the permeability, porosity and formation factor within the range of the measured values.

The velocity term U is controlled partly by the structure of the pore space. In media such as clay - rich Belly River sandstones the pore space may consist of macro-

and micro - porosity, (Iwuagwu and Lerbekmo, 1981). The average pore velocity of fluid flowing in such rocks would be the velocity in the macropores, as the fluid in the pore volume occupied by clay minerals containing micropores is assumed to be stagnant. Hence the average pore velocity, V_{mm} , is

$$U_m = (U/n)/r$$

$$V_{mm} = U_m(n_1/n_{mm}) \quad (34)$$

A general expression for the prediction of longitudinal dispersion of a tracer in clastic sandstones, therefore, would be

$$D_{11}/D_0 = 1/Fn + 0.5(V_{mm}d\sigma/D_0)^m \quad (35)$$

$$1.0 \leq m \leq 1.2$$

in which the value of m is dependent on the Pe régime. Values of D_{11}/D_0 and corresponding Peclet Numbers calculated with (35) for a range of V_{mm} using Data Set 5 are plotted on Figure 8. Inspection of the plot shows that these values are consistent with the trend of published experimental measurements on sandstone cores. The permeability of some of the samples in Data Set 5 is an order of magnitude lower than those used in the reported experiments. Since dispersivity is related to $\sqrt{k}$, it may reasonably be expected that these samples show decreased dispersion vis - á - vis the measured cores.

2.7 Models of Cation Exchange Capacity

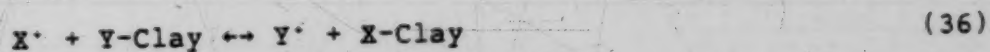
2.7.1 Cation Exchange on Minerals

Ion exchange is a term which describes the flow and counter flow of ions between a solution and the surfaces of a mineral, in the present case a clay. The ions are adsorbed on the ionic lattices of the mineral and are held there by electrostatic forces, so that the structure maintains electrical neutrality. The basic process can be considered as a chemical reaction of the form



in which X and Y are the exchanging ions. The structure and ionic charge of the mineral exchanger and the location and nature of the exchange sites, together with the pH, nature of dissolved ions, extent of association and activity coefficients in the surrounding solution affect the equilibria and kinetics of the exchange reaction. Hence the laws of physical chemistry and thermodynamics can be applied to the study of ion exchange and adsorption.

Ion exchange is a reversible process which can be described by the law of mass action. Consequently the exchange reaction of two univalent ions can be written as

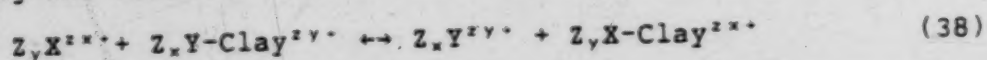


where X^+ , Y^+ are exchanging cations and X-Clay, Y-Clay are the ionic forms of the exchanger. From considerations of the law of mass action the thermodynamic exchange equilibrium constant K_X^Y takes the form

$$K_y^x = (a_y a_{x...}) / (a_{x...} a_{y...}) \quad (37)$$

where $a_{x...}$ and $a_{y...}$ represent the activities of the ions in solution, and $a_{x...}$, $a_{y...}$ are the activities of the ions in the exchanger. K_y^x is a constant for the particular ion exchange reaction and depends only on temperature.

It is convenient to derive an expression for the equilibrium constant in terms of the concentrations of the ions rather than their activities. To do this, rewrite (36) using the valences of the ions, ZX^+ and ZY^+ , obtaining



The equilibrium constant, K_y^x , is replaced by the *selectivity coefficient*, K_{xy} ,

$$K_{xy} = (m_y^{z^{x+}} m_x^{z^{y-}}) / (m_x^{z^{y+}} m_y^{z^{x-}}) \quad (39)$$

where m_i is the concentration of ionic species i in moles per unit weight on the exchanger, and m_i is a similar concentration in the solution. Note that in this homovalent case molality can be replaced by molarity or mole-fraction without changing the numerical value of K_{xy} . (Helfferich, 1962, p.154). K_{xy} is not a constant because it depends on the ratio of X to Y on the clay mineral exchanger, (Drever, 1982), and on the concentration of the surrounding solution, (Golubev and Garibyants, 1971). It is a measure of the preference of the clay exchanger for a particular ion.

Another means of expressing ionic equilibria is by use of the *distribution coefficient*, K_d , defined as

$$K_d = m_{xx} / m_x \quad (40)$$

where

m_{xx} = number of milliequivalents (meq) of ion X adsorbed per gram of exchanger

m_x = number of milliequivalents of ion X per milliliter of solution at equilibrium

(Reddy, 1977)

K_d increases as the solution becomes more dilute (m decreases) so that the equation shows that the quantity of an adsorbed ion which is present in trace amounts is proportional to its concentration in solution. (Helfferich, 1962; Drever, 1982).

Experimental determinations of selectivity are often expressed as *ion exchange isotherms*. These are plots of the equivalent fraction X_s of the ion X^{z+} in the solution against the fraction X'_s of the same ion on the clay exchanger at a given temperature. Various equations can be fitted to these isotherms to characterise the equilibrium partitioning of mass between a solution and a solid exchanger, (Gupta and Greenkorn, 1974).

Three commonly used types of adsorption isotherms are the linear, Freundlich and Langmuir isotherms, in which the amount of adsorbate on the adsorbent, F_s , is expressed, respectively by

$$k_1 C, k_2 C^n \text{ and } aC/(1+bC)$$

where k_1 and k_2 are the respective equilibrium adsorption constants for the linear and Freundlich cases; n , a and b are constants; and, C is the solute concentration, (Gupta

and Greenkorn, 1974).

The foregoing approach to ion exchange equilibria is based on the law of mass action. However the theory of the electrical double layer can be applied to determination of ion exchange equilibrium. Gapon(1933) considered cation exchange from the point of view of exchange between a surrounding solution and a monomolecular liquid layer adsorbed on a solid. He assumed that the quantity of a given liquid adsorbed by the solid varies with the surface area occupied by that liquid. Gapon's equation can be expressed as

$$K = C_2(f_1) / C_1(f_0 - f_1) \quad (41)$$

where f_0 is the total surface area, f_1 and f_2 are respectively the surface areas occupied by liquids C_1 and C_2 at equilibrium and K is a constant.

Gapon applied this equation only to binary exchange between monovalent and divalent cations. Such an equation for an equilibrium reaction which is based on a ratio of surface areas is



For this exchange Gapon found that

$$K = \sqrt{(C_2') \cdot (C_1') / (C_1)(CEC - C_1)} \quad (43)$$

where the prime (') indicates the adsorbed concentrations. Largerwerff and Bolt (1959) showed that K is constant only over the range of cation concentrations found in natural soils, and, in fact, varies with changes in the composition of the exchanger and the solution. It is thus analogous to

the selectivity coefficient derived from mass action considerations.

Cation exchange capacity is defined as the quantity of exchangeable cations required to maintain electrical neutrality of the mineral lattice, (Mitchell, 1976). CEC is expressed in the form of milliequivalents per 100 grams of dry exchanger. Another manner of expressing CEC is in terms of Q_v , the concentration of exchangeable ions per unit volume of material. CEC is related to Q_v by

$$CEC = [100n(Q_v)] / (1 - n)\rho \quad (44)$$

where

CEC = cation exchange capacity, meq/100g of dry rock

Q_v = concentration of exchangeable ions in pore fluid,
meq/mL

n = porosity of rock, fraction

ρ = grain density of rock, g/cm³

(Gall et al., 1983)

The CEC of various minerals is listed in Table 8. The high values for quartz reported by Carroll (1959) are inconsistent with the structure of the mineral and probably reflect the influence of trace quantities of amorphous silica or organic material. From a hydrogeological viewpoint the most important minerals involved in exchange reactions are the clay mineral groups listed in Table 2. The magnitude of CEC is related to the mechanism of exchange through the different strength of charges resulting from isomorphous substitution compared with broken bonds. Thus the smectites,

TABLE 8. CATION EXCHANGE CAPACITY OF VARIOUS MINERALS

Clay Mineral	CEC (meq/100g)
kaolinite	3 - 15
halloysite(2H ₂ O)	5 - 10
halloysite(4H ₂ O)	40 - 50
montmorillonite	70 - 120
illite	10 - 40
vermiculite	100 - 150
chlorite	10 - 240
glauconite	10 - ≥20
palygorskite grp.	20 - 30
allophane	25 - 70
quartz (2μm - 62μm)	0.6
quartz (<2μm)	5.3
quartz (4.4μm - 53μm)	<.01†
hydrous aluminium & iron oxides	4 *
feldspars	1 - 3 *
muscovite	1.8 **
calcite	<.01†
organic material	150 - 500 *

Sources:

Carroll (1959)

* Birkeland (1984)

** Perkins (1949)

†Beall and Allard (1981)

montmorillonite and vermiculite are characterised by a large CEC, whereas illite, kaolinite and chlorite have a small CEC. Mixed layer clays exhibit a CEC which is proportional to the content of pure end member components, (Manghnani and Hower, 1964; Hower and Mowatt, 1966). Other factors such as solution pH, particle size of the clay mineral and the valence and atomic weight of the exchanging cations also control the magnitude of CEC. The relationship between the structure and ion exchange characteristics of clay minerals has been summarised succinctly by Reddy(1977).

Certain cations can be adsorbed by clay minerals in a relatively immobile or fixed state. Robinson(1962) lists these cations as NH_4^+ , Cs^+ , Li^+ , Rb^+ , Ba^{2+} , Mg^{2+} and K^+ . The mechanisms of fixation are discussed by Sawhney (1972) and by Yariv and Cross (1979).

2.7.2 The Estimation of Cation Exchange Capacity

The use of Gapon's equation implies that the surface area of the exchanger is one of the factors controlling cation exchange. Both external and interlayer surfaces of minerals may be involved in cation exchange. The usual method of measurement is by the controlled sorption/desorption of a monolayer comprising molecules of known dimensions onto the solid exchanger. The surface area is calculated as the product of the number of molecules and their projected area. The theory and experiment of these techniques are adequately reviewed by various authors. (Ross and Olivier, 1964; Gregg and Sing, 1967; Parfitt and Sing, 1976; Sing, 1976; Greenland and Mott, 1978; Oscik, 1982).

These methods obtain the total surface area of the exchanger; in the case of clays which exhibit interlayer swelling this area includes the internal surface of the layers and that of the layer edges. Thus, the theoretical basal-face surface area of montmorillonite, calculated from its unit cell dimensions varies between $810\text{m}^2\text{g}^{-1}$ and $760\text{m}^2\text{g}^{-1}$, but the external surface area varies between $15\text{m}^2\text{g}^{-1}$ and $100\text{m}^2\text{g}^{-1}$, (Diamond and Kinter, 1958). Values of

surface area of different clays have been tabulated by Grim (1968), Diamond and Kinter (1958) and Van Olphen and Fripat (1979). Figure 9 shows that the CEC of shales, clays and sandstones is a function of their specific surface.

The surface area of the exchanger has been shown to be an important factor in determining its CEC. The samples from the Milk River, Erin and Morne L'Enfer Formations were used in conjunction with the data of Patchett (1975) to develop a relationship between CEC, specific surface and percentage of clay sized particles for silt- and clay- rich sands and sandstones. the proposed functional relationship is:

$$CEC = f(S_m, \%clay)$$

However, regression of the percentage of clay - sized particles against the specific surface of the samples from the dataset showed that these variables are highly correlated, ($r = .92$). It was found also that the specific surface was a better explanatory variable for CEC, so that the eventual fitted form of the relationship is:

$$CEC = .1872(S_m) - 4.059 \quad (45)$$

in which $r = .85$ However, to obtain values of specific surface for the sandstones of Table 5b a method using the percentage of clay and the assumed geometry of the clay particles is devised.

The method is similar to that used in the calculation of the external surface area, but the effective surface area available for cation exchange per unit mass, aS_m , is now the required quantity, in which a is a shape factor to be found

from the assumed geometry of the clay particles.

From Neasham (1977), the discrete particle clay is largely kaolinite; using the geometric approximation of cuboid blocks for the discrete particles of clay, the total external surface area exposed to cation exchange with the pore fluid would be five edge surfaces, so the shape factor becomes .833. Physically, ion exchange may be expected to take place also along the surface between the kaolinite booklet and the pore wall, but it is considered that such exchange would be negligible compared to that along the exposed edge surfaces of the booklet. The average reported specific surface area of well crystallised kaolinite is $35\text{m}^2\text{g}^{-1}$ by the BET method (Lea and Nurse, 1947), so that the effective surface area is $29.2\text{m}^2\text{g}^{-1}$. With the further assumption that the observed percentage of clay is equal to the proportion of pore space covered by the kaolinite, the specific surface area covered by the clay can be found.

For example, the clay - covered pore specific surface area of the Berea Sandstone of Table 5b is calculated to be $1.46\text{m}^2\text{g}^{-1}$. This value is multiplied by the complement of porosity to obtain the bulk specific surface area available for cation exchange. Hence the eventual estimate of the effective specific surface is $1.15\text{m}^2\text{g}^{-1}$. (44) is then used to compute CEC from the measured Q_v of each sample. Similar calculations for the pore lining and pore filling clays (assumed to be illite) gave the values of effective specific surface which are plotted on Figure 9. These values of

specific surface fall within the range of experimentally determined values for similar sandstones. All these values are plotted on Figure 5, which shows the relationship between specific surface and permeability.

If the concentration of all clays in a sample is known it is possible to estimate the CEC of the sample by a simple calculation of weighted proportions. Thus the averaged CEC of the pure clay mineral is weighted by its proportion and by the total concentration of exchangers in the sample. This procedure does not account for the possible contribution of organic materials or authigenic oxides and hydroxides of iron or aluminium to the CEC of a sediment. Nevertheless, where pure clay minerals are the major source of CEC the method gives acceptable results. Table 9 shows the match between the estimated and experimentally determined values of CEC for clay, clay- till and reworked loess samples from data in Gibb and Cartwright (1982). Table 10 shows the results for samples from the Milk River Formation of southern Alberta. All these samples are described in Appendices 1 and 2 respectively.

The method of weighted proportions may also be applied to mixed- layer clays. Data from a study by Mehra and Jackson (1959) of the structure and CEC of interstratified expanding clay minerals from various soils and sediments are plotted on Figure 10. The samples which contain vermiculite or illite as the major constituent and minor amounts of interstratified illite - chlorite, illite - montmorillonite,

TABLE 9. SIMULATION OF CATION EXCHANGE CAPACITY OF GLACIAL SEDIMENTS

Sample	C.E.C. (measured)	C.E.C. (calculated)
3-B9	7.7	9.31
3-B7	8.4	11.25
2-A56	5.4	11.69
2-A21	7.4	5.99
2-A4	9.2	14.19

Source: Gibb and Cartwright (1982)
(units of C.E.C. are meq/100g.)

illite - vermiculite and chlorite - vermiculite, plot as separate clusters in an intermediate position between pure vermiculite and montmorillonite on one end and pure illite on the other. The plot suggests that the CEC of a simple mixture of clays depends on the proportional mass present of each clay.

The data of Mehra and Jackson (1959) for complex mixtures of interstratified clays are examined to see whether the CEC of such materials is directly proportional to the composition of each component. Table 11 shows the CEC of various mixtures of interstratified clays measured by Mehra and Jackson (1959). These data can be analysed with CEC as the dependent variable by standard techniques for the analysis of mixtures described by various authors, (Scheffé, 1958; Snee, 1971, 1973; Cornell, 1973, 1979). Accordingly, a first degree polynomial of the form

$$Y = \beta_0 x_0 + \beta_1 x_1 + \dots + \beta_i + \text{error}$$

was fitted to the data. The equation for the response

TABLE 10. SIMULATION OF CATION EXCHANGE CAPACITY OF MILK RIVER FORMATION SAMPLES.

Sample Number	Rock Type	C.E.C. (measured)	C.E.C. (calculated)
2	siy sst	2.44	5.87
4	sst	2.86	2.65
5	sist	4.98	3.66
6	arg. sist	4.16	7.45
8	sist	0.89	0.44
9	sst	0.70	1.54
10	sdv sist	2.95	2.12
11	sst	2.44	8.09
12	arg. sist	6.45	2.45
13	arg. sist	5.75	7.81
14	arg. sist	5.55	8.63
15	arg. sist	4.02	7.19
17	arg. sist	7.54	9.33
18	sst	1.23	2.67
19	siy sh	14.46	13.78
20	siy sh	3.61	4.68
21	siy sh	6.72	10.89
22	arg. sist	6.68	7.78
24	arg. sist	6.62	8.98
27	arg. sist	8.14	8.58

Abbreviations:

sst = sandstone; sist = siltstone; sh = shale;
 arg. = argillaceous; siy = silty; sdv = sandy.
 (Units of C.E.C. are meq/100g.)

surface is

$$CEC = 175.34x_0 + 175.55x_1 + 214.13x_2 + 285.76x_3 + \text{error}$$

where

x_0 = fractional concentration of illite-chlorite

x_1 = fractional concentration of illite-vermiculite

x_2 = fractional concentration of chlorite -
 montmorillonite

x_3 = fractional concentration of illite-montmorillonite

The coefficients β_0 and β_1 are practically identical, suggesting that the effects of the concentration of illite -

chlorite and illite - vermiculite in the mixture are similar. Therefore the reduced equation

$$\text{CEC} = 175.42(x_0 + x_1) + 214.08x_2 + 285.74x_3$$

was fitted to the data. The fit is poor, with the adjusted coefficient of multiple correlation, $R^2 = .087$, and the equation is not significant. Physically, some of the variability in the data is due to the variation with layer composition of the charge balance and numbers of sites for isomorphous substitution of cations in the individual layers. Hence, the CEC response surface is not linearly related to the concentration of the components, and it appears to be impossible to derive a simple relationship between CEC and the overall mineralogical composition of mixtures of interstratified clays.

2.8 Discussion

New, empirical relationships have been developed in this study respectively between porosity, dispersivity and grain size distribution of a clastic sediment. Also, an empirical expression has been determined for relating the CEC of clastic sands and sandstones to their mineralogy. Further it has been shown that a simple extension of the Carman - Kozeny equation based on shape coefficients of mineral grains or pore linings can be used to estimate the permeability of such media. Nevertheless, the constraints attached to these predictors should be noted to prevent misapplication of the techniques.

TABLE 11. CATION EXCHANGE CAPACITY OF INTERSTRATIFIED CLAYS

Sample	% of Interstratified Clays				C.E.C.
	Ill-Chl	Ill-Vr	Chl-Mont	Ill-Mont	
2	0	100	0	0	156
3	15	15	15	55	300
4	20	60	0	20	233
5	50	0	50	0	191
6	66	0	34	0	200
7	66	0	0	34	168
8	33	33	34	0	157
9	100	0	0	0	216
10	100	0	0	0	177
11	50	0	0	50	183

Source: Mehra and Jackson (1959)
 Ill-Chl = Illite-Chlorite
 Ill-Vr = Illite-Vermiculite
 Chl-Mont = Chlorite-Montmorillonite
 Ill-Mont = Illite-Montmorillonite
 (units of C.E.C. are meq/100g.)

The constraints inherent in (2), (31) and (33) have been discussed immediately following the derivation of these equations and also in Appendices 1 and 2. In addition, use of (45) should be confined to clastic sands and sandstones in which the clay mineralogy is ascribed primarily to the kaolinite, illite, smectite and mixed - layer groups as defined in Table 2.

3. MODELLING MASS TRANSPORT IN SIMULATED MEDIA

3.1 Modelling Transport Parameters

3.1.1 The Estimation of Transport Parameters with GENPAR1 and GENPAR2

Solutions to (1) for the transport of reactive solutes in trace concentrations within saturated clastic sediments and sedimentary rocks require the realistic estimation of the controlling physical and chemical parameters. The constitutive relationships described in Chapter 2 provide a means for doing this from the more readily available data on the lithology and mineralogy of these classes of porous media. In this study, this goal is achieved conveniently through the use of two FORTRAN codes GENPAR1 and GENPAR2. The output from these programs provides the necessary parameters for the one- dimensional, analytical solutions and the two- dimensional numerical solutions to (1) which are described later in this Chapter for the determination of mass transport in simulated laboratory- scale columns and geologic sections composed of silty sands and clay- rich sandstones.

3.1.2 Description of GENPAR1 and GENPAR2

The constitutive relationships developed previously have been coded into a unified scheme for the estimation of the transport parameters of a sample of clastic sediment

from its lithology and mineralogy. Program GENPAR1 provides an estimate of the porosity, permeability, dispersivity and longitudinal dispersion coefficient (for the assumed fluid characteristics, head gradient and calculated fluid velocity) of a clastic sediment from its grain size distribution. The CEC and bulk density of the sample are calculated by the program from these properties assumed for the minerals constituting each size fraction. Program GENPAR2 estimates values of all the above parameters, except porosity, for a sandstone with authigenic minerals in the pore space. For this program it is considered that the effects of the grain size distribution are masked by the growth of authigenic minerals in the pore space. Consequently, size fractions are not used and the permeability and CEC are calculated directly from the mineralogy of the sample. However, the determination of dispersivity requires an estimate of the mean grain size of the rock. The total porosity must be estimated or measured independently, but the micro- and macro- porosity can be calculated by the program from the total porosity. Next, the permeability is calculated from the porosity, formation factor and properties of the authigenic minerals; this value of permeability is used in the computation of the dispersivity and related longitudinal dispersion coefficient. Finally, the bulk density and CEC of the sample is calculated from the properties of the minerals which constitute the fabric of the rock.

The primary input to GENPAR1 is a grain size distribution of the sediment that is represented by a weight fraction of each size class. The weight fraction of each class is expressed as a decimal fraction (i.e. the total weight of the sample is normalized to unity); the representative grain size of each class is calculated as the geometric mean of the upper and lower limits of that class. This approximation follows that of Fair and Hatch (1933) and is considered to be sufficiently accurate for the determination of specific surface. However, for greatest accuracy, the mean diameter should be converted to that of an equivalent sized particle with an average surface area, (Cadle, 1965; Beddow, 1980; Goldman and Lewis, 1984). The values of d_{80} , d_{10} and d_{50} and the uniformity coefficient can be calculated from the measured grain size distribution by subroutine CUMPAR, using linear interpolation between the cumulative size intervals of the distribution.

The porosity of the sample is computed in subroutine PORGEN, using (2) as the empirical predictive equation. The values of fines and size ratios required by PORGEN are calculated in the main program, together with the value for uniformity coefficient determined by CUMPAR. The estimates of porosity and uniformity coefficient are required for the calculation of permeability and of dispersivity by means of (12), (30) and (31) respectively.

There are two options for the computation of permeability within subroutine PERM1. The options are

selected by setting the variable IP to be zero or non-zero, respectively. The first option, with IP set to non-zero, uses (16) to calculate the specific surface from the mean grain size and shape coefficients of each of the sand-, silt-, and clay- sized fractions. Subroutine SHACOF is available to modify the size fraction shape coefficients to account for the differences in mineral composition. The second option, selected by setting IP to zero, calculates the specific surface based on the particle shape coefficient and proportional concentration of each mineral species present in every size fraction. In the usual situation of incomplete information on the mineral content of each size fraction, the first option will be selected. For this case values of the shape coefficients for the various size fractions are determined as outlined in Appendix 1.

The particle shape coefficient and proportional concentration of each mineral species also are utilised in the computation of the dispersivity of the sample in subroutine DISPR. They are used to calculate the variables G and x, which are required for the determination of the tortuosity, τ . The expression for the seepage velocity is modified from that presented by Harleman et al. (1963) by the inclusion of the tortuosity term. If the mineral content of the sample is not known in sufficient detail, G and x are considered to be given by the values for media comprised of cubes listed in Table 6. The fluid velocity is input to the calculation of the Peclet Number, Pe , which is the primary

selector for the particular equation used to determine the longitudinal dispersion, D_{11} , and hence the dispersivity, α_{11} , of the sample. The effects of the grain size distribution are modelled by means of the B parameter, which is functionally related to the uniformity coefficient and d_{50} , and is computed with (31).

It is necessary to know the mineral content of the various size fractions of the sample in order to calculate the bulk density and the CEC in subroutine CATPRP. The former is computed as the product of the weighted average of the density of individual minerals, $RHOAV$, and the complement of porosity; the latter is an average of the CEC of individual minerals weighted by their proportional concentration in the various size fractions.

The underlying premise of GENPAR2, in contrast to GENPAR1, is that the grain size distribution of a clastic sedimentary rock does not play a major role in controlling its hydraulic and transport behaviour. Instead, the porosity, specific surface and permeability of the rock are related to the amount and mode of occurrence of authigenic minerals within the pore space. Also, the properties of dispersivity and CEC are related to the permeability and specific surface of the rock. Accordingly, the primary input to GENPAR2 is a list of minerals which make up the fabric of the rock together with their specific surface, density, CEC and proportional concentration. The first three properties may be averaged quantities taken from published values, for

example in Grisak and Jackson (1978), or they may be based on actual measurements on samples of the particular class of porous medium being simulated.

It is not possible to derive a simple model for porosity in clastic sedimentary rocks: hence porosity must be determined from direct measurement on cores or from thin sections of rock. In the latter case the relationship derived in this study between the micro- and macro- porosity of clay- rich sandstones has been programmed into GENPAR2 for use in the calculation of permeability in subroutine PERM2, and dispersivity in subroutine DISPER. Alternatively, a representative value of porosity can be selected from a compendium of rock properties, for example Manger (1963) or Wolff (1982).

The calculation of permeability in subroutine PERM2 makes use of either (13) or (14) depending on the value of the Archie exponent, and with the required inputs of hydraulic radius, m , and formation factor, F , being computed with (17) and (19) respectively. The specific surface per unit mass of each mineral species, S_m , input in units of meters² per gram, is converted to the specific surface per unit volume, S_v , in units of centimeters² as the product of its density and proportional concentration.

The computed values of permeability and formation factor are used to solve (33) in subroutine DISPER to determine the characteristic length, d_0 . This value is input to (35) in order to calculate the longitudinal dispersion

according to the range of Peclet Number indicated by the fluid velocity in a manner analogous to the procedure adopted in GENPAR1. The mean grain size, d , is required for computation of the Peclet Number.

The calculation of bulk CEC with subroutine CATPP follows the general scheme of the equivalent subroutine of GENPAR1 with the important difference that the bulk CEC is determined from (45). For this equation, the specific surface per unit mass is used: hence the density of the mineral species is not required. The calculation of the proportion of CEC due to each mineral also is computed from its proportional concentration in a manner similar to that used in GENPAR1, but with the size fraction implicitly set to unity.

Listings of GENPAR1 and GENPAR2, and examples of their usage are presented in Appendix 3. Schematic flow charts of the programs also are presented in Appendix 3.

3.1.3 Applications of GENPAR1 and GENPAR2

In this section I demonstrate the application of these two codes to the generation of the hydraulic and transport parameters for both artificial and natural porous media.

The artificial media to which GENPAR1 is applied are designed to have specified ranges of uniformity coefficient for each value of d_{50} . The grain size distributions of these media are tabulated in Appendix Table A3.2.1. The grain size distributions were also designed to have the nominal values

of RFF of 20, 100 and 500. These parameters are listed in Appendix Table A3.2.2. The d_{50} of each notional sample was chosen to be characteristic of medium sand, very fine sand and silt respectively.

The grain size distributions of the simulated media are typical of natural sediments from various depositional environments which are not characterized by a log-normal distribution of particle sizes, (Moss, 1962, 1963; Spencer, 1963; Visser, 1969; Glaister and Nelson, 1974). The apparently non-lognormal shape of many grain size curves are explained as mixtures of more than one log-normal population, each of which reflect the differing mode of transport of different sizes of sediment. Also, in some environments the parent population may be censored or truncated by the sediment transport process, (Tanner, 1964). Thus, the distributions used in the study are realistic and are designed to show the effects of the grain size parameters on the hydraulic and transport properties of clastic sediments. Subsequent simulations are designed to demonstrate the added influence of clay minerals in the silt- and clay- sized fractions on these properties. The silt and clay size composition of the simulated sediments are summarized in Appendix Table A3.2.3.

The effects of uniformity coefficient, size range and d_{50} on porosity, permeability and dispersivity for sands containing no clay minerals are illustrated in Figures 11, 12 and 13 respectively. The model successfully predicts the

increase in porosity shown by real, loose- randomly packed sediments with increase in the silt content. Similarly, the direct relationship between d_{50} and permeability is clearly shown in Figure 12. Also, a similar relationship is demonstrated by Figure 13 for dispersivity.

Figure 11 graphically illustrates the influence of the proportion of silt and clay sized particles, RF, upon the porosity of the simulated sediments. At low values of RF the effects of a high uniformity coefficient, ($UC = 5$), coupled with values of RFF of 100 and 500 are to reduce the porosity of coarse- grained sediments, with a d_{50} of 0.15 cm and 0.04 cm respectively. The physical explanation of this observation is that at the larger spread of sizes of the material, corresponding to higher values of RFF, the small volume of silt and clay sized particles can pack between the larger grains and hence reduce the porosity slightly. At higher values of RF, resultant upon the increase in the volume of silt and clay in the mixture, the porosity increases because of the change to flocculated, "house- of- cards" types of structures within the clay particle aggregates. Thus, at very high values of RF the effects of UC and RFF are masked by those created by the packing structure of the particles.

Figure 12 illustrates the strong influence of the d_{50} of a clastic sediment upon its permeability. There is a decrease of nearly four orders of magnitude in permeability from $1E-5$ cm² to about $3E-9$ cm² to accompany a decrease in

mean grain size from .15 cm to .0015cm. Within each size class, the highest permeability is characteristic of the best sorted sands as typified by the lowest values of uniformity coefficient and ratio of largest to smallest size, (UC = 1 and RFF = 20). The actual spread of values is variable within each size class and is related to the variation in the specific surface due to the differing amounts of the finest sized materials.

Figure 13 shows that the magnitude of the d_{50} also strongly influences the dispersivity of the sediment, but the relationship is an inverse one. In this case the highest dispersivity is characteristic of the least well sorted sands as typified by the highest values of uniformity coefficient and ratio of largest to smallest size, (UC = 5 and RFF = 500). The actual spread of values is relatively constant within each size class because the governing equation, (31), is defined in terms of UC and d_{50} only.

The role of clay minerals in the clay- and silt- sized fractions in modifying the hydraulic and transport properties of a clastic sediment is examined by introducing various percentages of clay minerals into each notional sample. The percentages are set at 2, 5 and 10 in the silt fraction and are coupled with percentages of 20, 50 and 100 in the clay fraction. These proportions are based broadly on charts and tables in Kovacs (1981) and Gheorghe (1979), which show the generalized mineral composition of the sand-, silt- and clay- sized fractions of fluvial- alluvial clastic

sediments.

Two series of simulations are performed: one with single clay minerals and the other with a simplex of kaolinite, illite and montmorillonite.

The results of the simulations with single clay minerals are displayed in Figures 14, 15 and 16. The reduction in permeability with increasing percentages of montmorillonite in silt-sized sediments is clearly shown; the concomitant increase in dispersivity is less dramatic. Figure 15 shows that the CEC is directly proportional to the concentration of the individual clay mineral in each size fraction. Hence, for example, the CEC of Run 8B with montmorillonite is equivalent to Runs 10 and 11B with illite, and is slightly greater than Run 12B with kaolinite.

Figure 14 displays the effect of various percentages of different clays upon the permeability and dispersivity of the simulated sediments. In the coarser grained material, exemplified by Runs 8B, 9B and 10, the influence of grain size is seen to be paramount, so that increasing the amounts of clays as described has an insignificant effect on the permeability and the dispersivity of these sediments. However, in the finer grained material of Runs 11B and 12B, the increased quantity of clay causes a measurable decrease in the permeability and increase in the dispersivity. The magnitude of the change depends on the composition of the clay, being greatest for montmorillonite and least for kaolinite.

The bulk density of a sample is computed as the product of the averaged grain density of the minerals in all size fractions and the complement of porosity. Hence it is strongly related inversely to the higher porosity of the silt samples of Runs 10, 11B and 12B. Also, except for illite, the assumed density of the minerals is close to that of quartz, so that there is little variation with percentage of montmorillonite and kaolinite.

The effect of clay mineral composition on permeability is modelled here only by varying the shape coefficient ascribed to individual clay species according to the methodology described in Chapter 2 and Appendix 1. Reduction in permeability with time due to the swelling or movement of clay minerals in the pore space is not included in the model. Lovas (1963) observed this effect in sand columns with interstitial clay. These experimentally observed reductions in permeability occurred over a period of less than about 70 hours, whereas the purpose of the model is to generate parameters for simulating steady-state mass transport over a longer time period. Also, since the salinity of fluids is assumed to be constant, the variation of permeability with salinity observed elsewhere (McNeal and Coleman, 1966; Frenkel et al., 1978; Goldenberg et al., 1984) is not considered further.

The simulated responses of various mixtures of illite, montmorillonite and kaolinite in Runs 11B and 12B are graphed in Figures 17 and 18. The composition of the clay

mineral simplex is listed in Table 12. The permeability is seen to be related to the concentration of montmorillonite in the mixture; thus, the value of permeability for the mixtures is similar to the permeability of the run with only montmorillonite. A similar but inverse relationship is observed for dispersivity, consequent upon the dependence of this parameter on permeability. Also, since the bulk CEC is proportional to the concentration of individual clays, the simplex shows a simple, linear response surface for the various mixtures of Runs 11B and 12B.

Next, we consider the application of GENPAR1 to the estimation of the transport parameters for a real medium. The properties of a typical Milk River Sandstone outcrop sample as described by Meyboom (1960) are listed in Appendix 1. Because the sandstone is friable to poorly cemented it is reasonable to assume that the grain size distribution and detrital mineralogy of the rock are the main controls on its hydraulic characteristics. The predicted porosity and permeability are 0.31 and 7.3 millidarcies. No data are available for porosity but the permeability value falls within the range reported for horizontal and vertical permeability laboratory determinations and pumping tests of water wells reported by Meyboom (1960). Values of porosity and permeability respectively of 0.17 to 0.26 and 2.75 millidarcies to 259 millidarcies are given by Meijer Drees and Myhr (1981) from laboratory measurements on cores from wells in the Alderson member of the Lea Park Formation,

TABLE 12. COMPOSITION OF CLAY MINERAL SIMPLEX, GENPAR1 SIMULATIONS

Mineral Combination	Mineral		
	Montmorillonite	Kaolinite	Illite
1	.10	.80	.10
2	.10	.45	.45
3	.45	.45	.10
4	.34	.33	.33
5	.10	.10	.80
6	.45	.10	.45
7	.80	.10	.10
8	.23	.54	.23
9	.23	.23	.54
10	.54	.23	.23

which is the down-dip equivalent of the Milk River Sandstone.

There are no measurements of dispersivity against which to compare the predictions of this quantity, but inspection of Figure 8 reveals that the trend for the Milk River Sandstone, estimated from GENPAR2, conforms to the general relationship for dispersivity of sandstones. GENPAR2 is used because the presence of authigenic minerals and cements implies that the dispersivity would be more accurately predicted from (35) than (31) and (32). In this case the formation factor includes the effect of the very fine matrix which is not adequately described by the mean grain size and uniformity coefficient of the disaggregated grains.

My experimental determinations of the bulk CEC on cores from the Alderson member, listed in Appendix 1, average 4.9 meq/100g., with a range of 0.89 meq/100g. to 14.46 meq/100g. The estimate of 1.1 meq/100g, computed for the typical Milk

River Sandstone falls within this range.

GENPAR2 is applied in a similar manner to the prediction of the mass transport properties of the Belly River Sandstones described by Iwuagwu (1979) and Iwuagwu and Lerbekmo (1981). Table 13 shows the formation factor, dispersivity, specific surface and bulk CEC predicted by GENPAR2 from the porosity, permeability, mean grain size and clay- sized mineral abundance data listed in Appendix 1. The calculated formation factor of each sample falls within the range of those measured on a wide range of sandstones, for example those listed in Fatt (1958). The use of these estimates of formation factor coupled with the measured values of porosity, macro- porosity and permeability resulted in the predicted values of dispersion plotted on Figure 8. These values are in the general range for sandstones.

The permeability predicted for the Belly River Sandstones from the assumed shapes of the pore- lining and pore- filling minerals is compared in Table 7 with the measured values. Generally the match is close because, despite the poly- mineralic nature of the authigenic mineral suite, the most important control of permeability is the presence of pore- filling kaolinite. Thus, use of the technique, described in Appendix 1, for estimating the effective specific surface of kaolinite was successful in predicting permeability. In some instances, for example samples 14 and 16, large amounts of secondary calcite have

TABLE 13. SIMULATION OF PETROPHYSICAL PARAMETERS OF BELLY RIVER SANDSTONES.

Sample Number*	Formation Factor	Dispersivity (cm.)	C.E.C. (meq/100g.	Specific Surface m. ² /g.	Bulk Density g./cm. ³
8	15.36	0.285	0.593	0.852	2.291
9	19.12	0.388	0.791	1.579	2.327
10	136.49	2.946	1.378	2.312	2.487
11	20.85	0.426	0.958	2.078	2.300
12	15.97	1.287	0.837	1.709	2.393
13	96.47	13.880	1.128	2.381	2.453
14	118.21	14.990	2.559	1.914	2.680
15	30.772	0.631	0.772	1.220	2.280
16	43.491	2.852	2.146	1.669	2.527
17	9.293	0.149	0.780	1.074	2.169
18	20.048	0.403	0.882	1.598	2.326
19	28.172	0.587	1.253	2.230	2.355
20	19.361	0.394	0.941	1.923	2.350
21	13.552	0.261	0.830	1.498	2.337
22	16.412	0.326	0.916	1.657	2.353
23	16.683	0.326	0.757	1.175	2.273
24	26.663	0.548	0.903	1.684	2.337
25	25.457	2.506	1.015	2.256	2.392
26	58.636	1.248	1.268	1.663	2.375
27	39.300	0.828	1.230	2.449	2.404
28	43.398	2.220	0.991	1.884	2.546
29	16.160	0.316	0.721	1.086	2.275
30	11.294	0.202	0.722	0.986	2.202

*Source: Iwuagwu (1979).

plugged the pore space and reduced the permeability by reducing the porosity to very low values.

Iwuagwu (1979) notes from SEM evidence that rosettes and fan-shaped clusters of chlorite occur irregularly in the samples together with plates and flakes of illite-montmorillonite. The presence of these minerals, which are not estimated volumetrically by Iwuagwu (1979), may explain some of the discrepancies between the predicted and measured permeabilities. Similarly, if these minerals are taken into

account, the apparently anomalous plotting positions of the Belly River samples on Figure 9 may be explained. Iwuagwu (1979) indicates that the authigenic minerals occur as pore-lining and pore-bridging clays rather than as discrete particles. By including the average specific surface and CEC of chlorite and illite-montmorillonite on a mass proportional basis the plotted position of the Belly River Sandstones would be expected to shift towards the positions of the pore-lining and pore-bridging clays on Figure 9. This shift would result from the greater relative increase in specific surface vis-à-vis the bulk CEC for illite-montmorillonite and chlorite.

3.2 Simulation of Mass Transport in Adsorbing Media

3.2.1 Modelling Transport with Complex Ion Exchange

Earlier in this Chapter, it has been shown how important clay minerals can be in controlling the variability of key transport parameters. With the application of mass transport modelling it is possible to examine how changes in sets of transport parameters influence the migration of ions in groundwater.

In addition to the development of techniques for modelling the various transport parameters, a major emphasis in this thesis is to extend modelling approaches to include complex exchange processes. Accordingly, an important component of this work involves the development and

verification of a multi- component, multi- exchanger model for this purpose.

Previous studies concerned with modelling the influence of ion exchange in mass transport focus mainly on the integration of empirical approaches involving various exchange isotherms into mainly one- dimensional transport models. The development of these basic concepts for linear, Langmuir and Freundlich exchange isotherms as well as problems involving non- equilibrium exchange and exchange with hysteresis are discussed in detail by Cleary et al. (1981) and Van Genuchten and Cleary (1979). These approaches have been particularly useful in developing an improved understanding of how sorption influences the spread of a contaminant, (see for example, Freeze and Cherry, 1979). However, the empiricism, the inability of these analytical or semi- analytical approaches to account for spatially varying parameters, and the difficulty of solving multi- dimensional problems have limited their practical usefulness.

There have been some efforts to adapt the more rigorous thermodynamic approaches to ion exchange into numerically based models that could potentially be applied to field problems. However, considering the importance of ion exchange as an attenuation mechanism for the spread of contaminants, these kinds of studies are not abundant. The most important early work is that of Rubin and James (1973), who developed a one- dimensional, finite element model for

exchange affected transport. Their model assumed the steady flow of groundwater and binary or multicomponent ion exchange defined by a constant or concentration- varying selectivity coefficient. Although the inability to generalize the finite-element procedure to more than one dimension limited the practical applicability of the approach, the theoretical framework for ion exchange developed by Rubin and James (1973) formed the basis for several subsequent studies.

Schwartz (1975) incorporated binary exchange concepts into a two- dimensional model for contaminant transport in regional groundwater flow. This study provided the first practical model for evaluating simple exchange- affected transport in complex hydrogeological settings and the first systematic attempt to evaluate the role of major transport parameters in controlling the spatial manifestation of contaminant plumes. Valocchi et al. (1981) developed a one- dimensional simulational model that is very similar to that of Rubin and James (1973) to investigate both theoretical and practical aspects of ion exchange. They applied the model to a field problem involving the injection of municipal sewerage effluent into an aquifer to confirm the validity of chromatographic theory for field- scale transport problems.

The models developed by Rubin and James (1973), Schwartz (1975) and Valocchi et al. (1981) are examples of what Miller and Benson (1983) describe as one- step

procedures for solving mass transport equations. Ion exchange is included directly in a system of equations describing the physical and chemical transport processes. These equations are solved simultaneously in one step to yield concentration distributions in space and time. Miller and Benson (1983) consider this procedure to be the most rigorous mathematically, but concede that the computation is tractable only for one-dimensional problems.

The application of Schwartz (1975) to two dimensions is successful because the special case of binary exchange is computationally much simpler to handle. The one-dimensional, finite-difference transport model developed by Miller and Benson (1983) is clearly the most sophisticated example of this procedure that has been developed to date. Their code accounts for advection, dispersion and complex chemical reactions including aqueous phase complexation, and exchange of both ions and complexes. A later extension of their model reportedly includes chemical precipitation and a model of sorption which includes surface ionization and complexation for solids whose surficial site density varies as a function of pH.

In the two-step procedures, the processes of physical and chemical transport are handled separately. Mass concentrations are determined initially as a solution to the advection-dispersion equation, and subsequently corrected to account for the partitioning of mass due to equilibrium ion exchange. Although this procedure is considered

theoretically to be less rigorous than the one- step approach (Miller and Benson, 1983), it is simpler computationally. This simplicity facilitates its application to very complex, two- dimensional, multi- component systems.

The number of these models that have been developed to date is also very limited. Ahlstrom et al. (1977) discussed briefly how such a model with multi- component exchange could be developed in conjunction with a moving particle approach for solving the advection- dispersion problem. However, I have not found any recent work which suggests that such a model has been developed. In addition, a very extensive set of numerical experiments has been carried out as part of this thesis using a moving particle approach similar to that described by Ahlstrom et al. (1977). The results of these trials strongly suggest that the moving particle method is not sufficiently accurate to incorporate complex ion exchange processes. Small statistical fluctuations inherent in this method are amplified during the second or equilibration step to the extent that in some cases the solution becomes grossly inaccurate.

Actual applications of the two- step procedure to multi- dimensional, multi- component transport are discussed by Dudley et al. (1981) and by Schultz and Reardon (1983). Dudley et al. (1981) extended the testing of the model SALTFLO, developed by Robbins et al. (1980a,b), to studies of the leaching of soil plots by irrigation water. SALTFLO simulates the one- dimensional transport of eight major ion



species in a soil containing lime and gypsum. The model accounts for advection and dispersion, multicomponent ion exchange and the dissolution and precipitation of lime and gypsum. Schultz and Reardon (1983) couple a two-dimensional, mixing cell model, which provides a solution to the physical transport problem, with an equilibrium chemical model incorporating multi-component, cation exchange and calcite equilibria. They use this simulation procedure to match closely the variation in six ions observed during a field dispersion experiment.

This examination of previous studies has shown firstly the difficulty in dealing with multi-component problems in more than one dimension, and secondly, the very limited number of studies in this general area. The simulation approach, which is developed in the following sections of this chapter, will be a major extension of two-step methodology to the examination of two-dimensional, multi-component transport with multiple exchange reactions.

3.2.2 Mathematical Approach

To describe the distribution of contaminants as a function of space and time requires the solution to a system of partial differential equations similar in form to (1). In general, one equation is written for each component with particular terms in the equation accounting for the major transport processes of interest. These processes and most of the parameters characterizing them have been considered in

detail in Chapter 2. However, the velocity terms in (1) require further examination.

The terms v_x and v_y define the velocity of groundwater flow in the two coordinate directions. It is through these two terms that the mass transport processes are coupled to actual groundwater flow. Values for these terms can be specified in two different ways. For very simple groundwater flow systems, velocities can be specified as single-valued constants across the two-dimensional space. For more complex flow systems where velocities vary from point to point, the problem of specifying the variation is more difficult. A groundwater flow model must typically be used in these cases to simulate the flow pattern from which the required velocity field is determined. The model developed here is sufficiently general to handle either constant or spatially varying velocity fields. However, to reduce the complexity of the code a flow model is not included, as is the case in some studies, (Schwartz and Crowe, 1980). Instead, velocity values are specified as input. Thus, implicit assumptions in my approach are that:

- (a) the groundwater flow is steady, and
- (b) patterns of groundwater flow are not influenced by changing ion concentrations within the flow field.

These assumptions are reasonable simplifications which are made in most model developments.

Having developed the transport equations from (1), the next major step involves their solution. The two-step

procedure as I have discussed earlier very conveniently enables the physical transport processes to be separated from the ion exchange processes. For this reason, the description of the numerical approach will consider firstly the solution of the transport equation with only advection and dispersion, then secondly how several ionic constituents are partitioned among several exchangers, and finally how the two steps are integrated into a complete modelling package.

3.2.3 Solutions to the Advection- Dispersion Equation

Numerical approaches for solving the advection-dispersion equation can be divided into two main classes, (Neuman, 1979). When both dispersive and advective processes are important in (1), the equation has a parabolic form. As convection dominates over dispersion, i.e. the dispersion coefficients become small, the transport equation behaves more like a hyperbolic equation. Well-known numerical approaches for solving partial differential equations such as the techniques of finite differences or finite elements, typically work well only for equations that are parabolic in form. For near-hyperbolic equations, which describe the behaviour of commonly observed phenomena in the field, these solutions exhibit a variety of problems. These include numerical oscillations, overshoot or undershoot and numerical dispersion. In severe cases, these problems can result in wildly inaccurate solutions to the equations.

These difficulties provided the impetus for the development of numerical procedures that are more directly suited to the solution of the hyperbolic form of the transport equation. The best known of these are the discrete-parcel-random-walk (DPRW) method, (Ahlstrom et al, 1977; Schwartz and Crowe, 1980), and the earlier developed method of characteristics (MOC), (Garder et al, 1964; Pinder, 1973; Schwartz, 1975). Both of these techniques avoid the previously discussed numerical problems and have worked well in practical applications. Nevertheless, there are other problems, such as the logistics of keeping track of swarms of reference particles in the flow field, mass balance errors due to uneven particle distributions, and limitations on time step size as a requirement for numerical stability. These problems require careful coding to prevent inaccuracies in the numerical solution.

The MOC is used in this study to solve the advection-dispersion equation. Because the details of the theory are presented elsewhere, (Reddell and Sunada, 1970; Konikow and Bredehoeft, 1978), only a brief discussion of the procedure will be given here. The approach taken in MOC is to solve an equivalent set of ordinary differential equations (ODEs) instead of solving the advection-dispersion equation directly. Mathematically this procedure can be represented as follows:

$$\partial C / \partial t + v_x [\partial C / \partial x] + v_y [\partial C / \partial y] = f(x, y, t) \quad (46)$$

where C is the concentration of the contaminant, x and y are the space coördinates, and t is time. This equation can be replaced by the following set of ODEs:

$$dx/dt = v_x ; dy/dt = v_y ; dC/dt = f(x,y,t)$$

The first two ODEs yield the position of fluid particles which are being convected by groundwater along streamlines. In the actual modelling approach this component of transport is accounted for by the motion of a set of moving reference particles with some attached concentration, which varies as a function of time. During each time step in a transient simulation, the reference particles are transported along a streamline for a distance determined by the magnitude of the seepage velocity. For each cell in a rectangular grid system, a concentration is calculated by averaging the concentration of reference particles located in the cell. The influence of dispersion on the concentration distribution is accounted for by solving the ODE for the time concentration, dC/dt . Changes in the mean concentration of components within individual cells are also assigned to the reference particles located in the respective cells. Thus, particle motion in the next time step will include the previous dispersion.

The main reason for the success of the MOC is that when dispersion essentially is negligible the concentration-time ODE simply tends to zero without any effect on the solutions to the first two ODEs. Also, solutions to (46), which is essentially a diffusion equation, are relatively stable

numerically. In my development of the method, an explicit, centered- in- space, finite difference procedure is used to solve the dispersive spread within the system. The actual form of the finite- difference equation is identical to that described by Reddell and Sunada (1970).

My approach differs from all other published implementations of the MOC in the extension to handle more than one dissolved constituent. This change requires that moving reference particles carry more than one concentration and that the finite- difference procedure is applied to an uncoupled system of ODEs.

3.2.4 Modelling Equilibrium Ion Exchange

Within every time step in the MOC solution to (1) it is necessary to account for the equilibrium redistribution between the solution and the solid phase. The procedure developed here formulates cation exchange by means of the Gapon convention described by (41), (42) and (43). These equations are written for two exchanging cations on a single exchanger, but the equations developed here can account for the exchange of n cations on m exchangers. The theory uses concepts outlined by Robbins et al. (1980a,b) and Sposito (1981).

The model is designed to describe the exchange of a trace contaminant T_i^+ with two macroscopic counterions M_1^+ and M_2^+ . Following Robbins et al. (1980a,b) it is possible to write one equation to express a mass balance of ions on

the exchanger. The exchange equations follow the form of (42) for the case of heterovalent cation exchange. It is assumed that the cations are the only ones present in the fluid in significant quantity and that their sum is the CEC. Hence

$$(CEC)_i = M_{3^+} + M_{2^+} + T_{1^+} \quad (47)$$

where

M_{3^+} , M_{2^+} , T_{1^+} = concentration of M_{3^+} , M_{2^+} , T_{1^+} (meq/100g)

$(CEC)_i$ = total CEC of exchangers

Using the Gapon convention, the selectivity coefficients for each exchange reaction on individual exchangers are found to be

$$K_{11} = \{[(M_{3^+})M_{2^+}]/[(M_{2^+})M_{3^+}]\}_i \quad (48)$$

$$K_{21} = \{[(T_{1^+})M_{3^+}]/[(M_{3^+})T_{1^+}]\}_i \quad (49)$$

$$K_{31} = \{[(M_{2^+})T_{1^+}]/[(T_{1^+})M_{2^+}]\}_i \quad (50)$$

where

(M_{3^+}) , (M_{2^+}) , (T_{1^+}) = concentrations in solution of M_{3^+} , M_{2^+} , T_{1^+} respectively,

K_{11} , K_{21} , K_{31} = selectivity coefficients of $M_{3^+} - M_{2^+}$, $T_{1^+} - M_{3^+}$, $M_{2^+} - T_{1^+}$ exchange reactions respectively on the i th exchanger.

To solve for each of the exchangeable cations, one rewrites each equation in which the cation of interest occurs in terms of the other cations. Thus, to solve for T_{1^+} , solve (49) and (50) for M_{3^+} and M_{2^+} respectively to obtain

$$[M_{3^+}]_i = \{[(M_{3^+})T_{1^+}/K_{21}(T_{1^+})]\}_i \quad (51)$$

$$[M_{2^+}]_i = \{[(M_{2^+})T_{1^+}/K_{31}(T_{1^+})]\}_i \quad (52)$$

Next, (51) and (52) are substituted into (47):

$$[\text{CEC}]_i = \{T_i^* + [(M_3^*)T_i^*/K_{2,i}(T_i^*)] + [(M_2^*)T_i^*/K_{3,i}(T_i^*)]\}, \quad (53)$$

Dividing through by T_i^* , we obtain

$$[\text{CEC}/T_i^*]_i = \{1 + [(M_3^*)/K_{2,i}(T_i^*)] + [(M_2^*)/K_{3,i}(T_i^*)]\},$$

$\therefore$

$$[T_i^*]_i = \{(\text{CEC})/1 + [(M_3^*)/K_{2,i}(T_i^*)] + [(M_2^*)/K_{3,i}(T_i^*)]\}, \quad (54)$$

Similar expressions are obtained for M_3^* and M_2^* :

$$[M_3^*]_i = \{(\text{CEC})/1 + [K_{1,i}(M_2^*)/M_3^*] + [(T_i^*)/K_{2,i}(M_3^*)]\}, \quad (55)$$

$$[M_2^*]_i = \{(\text{CEC})/1 + [M_2^* \cdot (M_3^*)/K] + [K_{3,i}(T_i^*)/(M_2^*)]\}, \quad (56)$$

(54) through (56) are summed over all the exchangers to obtain the adsorbed concentrations of the cations.

In the past ten years, there has been a considerable effort in developing approaches to solving (54) through (56). The most important procedures, which are summarized in Kincaid et al. (1984) include:

- (a) optimization methods;
- (b) solution of non-linear equations; and
- (c) miscellaneous methods.

The iterative procedure developed here appears to fall into group (c) of Kincaid et al. (1984). It is an interval halving technique where the initial estimate of the concentration of ions in solution is refined through a series of iterations.

The first step in the procedure involves establishing the total mass of individual ion species in the solution and adsorbed on the exchanger(s) before equilibration. This ultimately provides the criteria to test successive estimates of the equilibrium mass distribution. The second step involves providing an initial guess of the concentration of (T_1^*) , (M_2^*) and (M_3^*) in solution. In most cases, the choice of this starting value is problem dependent but usually involves decreasing (T_1^*) to one half of its unequilibrated value and increasing (M_2^*) and (M_3^*) by an amount appropriate to their relative abundances. Given estimates of ion concentration in solution, it is possible as the third step to solve (54) and (56) and to calculate $[M_3^*]$, in (55) to estimate the ion concentration on the exchangers. The fourth step establishes the mass balance for individual ions in the system given concentrations of ions in solution and on exchangers from the second and third steps. The fifth step compares the newly calculated distribution with that in the first. Based on this comparison, the guess of (T_1^*) , (M_2^*) and (M_3^*) concentrations in solution is refined with the return to the second step. The iteration continues in the second through fifth steps until a specified convergence criterion is met. At this point, the calculation yields the equilibrium concentration of ions in solution and on the exchangers.

In most cases, convergence is achieved with this procedure in about 30 to 40 iterations. Although this

approach is numerically unsophisticated and computationally inefficient relative to other techniques, it is relatively simple to code and appears to converge well for a small number of components.

The ion exchange model has been verified in an application involving the simulation of the experimental study of the exchange adsorption of Cs^+ on montmorillonite, kaolinite and illite in the presence of competing Na^+ , performed by Wahlberg and Fishman (1962). In the experiments the clay is saturated with 3M NaCl solution; a 100 milligram sample of clay ground to pass a 100 - mesh sieve is exposed to a 10 ml solution with various known concentrations of Cs^+ and Na^+ . Wahlberg and Fishman (1962) presented their results in the form of graphs of the distribution coefficient, K_d , and Cs^+ concentrations for NaCl solutions of varying normality. For these systems the mass action equation can be written as



The selectivity coefficient, K' , and the distribution coefficient, K_d , for this reaction would be, respectively

$$K' = [\text{XCs}(\text{Na})]/[\text{XNa}(\text{Cs})] \quad (58)$$

and

$$K_d = \text{XCs}/(\text{Cs}) \quad (59)$$

Wahlberg and Fishman (1962)

(58) and (59) may be combined in order to obtain an expression for K_d in terms of the concentration of Na^+ :

$$K_d = K' \text{XNa}/(\text{Na}) \quad (60)$$

For trace concentrations of Cs^+ , (58) may be rearranged to yield the following expression for K' :

$$K_s = K' (X_{\text{Na}} + X_{\text{Cs}}) / (C_s + N_a)$$

$$\therefore K' = K_s (\text{CMEQ})_s / \text{CEC} \quad (61)$$

where

$(\text{CMEQ})_s$ = total concentration of Cs^+ and Na^+ in solution, meq/l

CEC = cation exchange capacity of the exchanger, meq/100g.

For larger concentrations of Cs^+ , K' can be found from an equation reported by Grisak and Jackson (1978):

$$K' = K_s \{ [(\text{CMEQ})_s - (C_s)] / [\text{CEC} - (X_{\text{Cs}})] \} \quad (62)$$

Values of K' are calculated with either (61) or (62), as appropriate, and used as input to the cation exchange routine together with the concentrations of Cs^+ and Na^+ and the CEC measured by Wahlberg and Fishman (1962). The routine returns equilibrium concentrations of Cs^+ and Na^+ , and values of K_s . These results are tabulated in Tables 14 and 15. The match between the observed and simulated values of K_s is fair for trace concentrations of Cs^+ , but is poor at greater concentrations of Cs^+ , especially for simulation runs 12, 13, 19 and 20. Concentrations of Cs^+ for these runs would appear to be outside the range of validity of (61) and (62).

Wahlberg and Fishman (1962) noted that their values for K_s , calculated from (59), were consistently lower than those which are experimentally determined. They suggested that a

TABLE 14. RESULTS OF SIMULATION OF EXCHANGE ADSORPTION OF CESIUM ON MONTMORILLONITE

Exchanger: Na-Montmorillonite No.11 (C.E.C.=116 meq/100g.)
Exchanging Cations: Cs-Na

Simulation Run	Conc. of Cs, mmol	Conc. of Na, mmol	K' (Cs)	K _d
1	1.0E-7(1E-7)	2.0(2.0)	5.17E4	4.6E4(3E4)
2	9.99E-3(1E-4)	2.0(2.0)	1.21E4	1.89E4(9E3)
3	1.0E-7(1E-7)	10.0(10.0)	6.03E4	1.89E4(7E3)
4	5.97E-5(6E-5)	10.0(10.0)	6.03E4	1.88E4(7E3)
5	2.99E-3(3E-3)	10.0(10.0)	6.03E4	1.89E4(7E3)
6	5.01E-2(5E-2)	10.39(10.0)	5.20E4	1.54E4(6E3)
7	3.07E-1(3E-1)	10.63(10.0)	4.45E4	1.18E4(6E3)
8	9.99E-6(1E-7)	100.0(100.0)	8.62E4	2.7E3(1E3)
9	1.12E-3(1.2E-3)	100.0(100.0)	6.90E4	2.15E3(8E2)
10	7.99E-2(8E-2)	100.1(100.0)	6.47E4	1.97E3(7.5E2)
11	.6994(.7)	100.7(100.0)	5.21E4	1.26E3(6E2)
12	1.96(4.0)	102.0(100.0)	82.76	9.56(5E2)
13	2.97(30.0)	12.97(10.0)	8.62	1.1(2E2)
14	9.99E-6(1E-7)	200.0(200.0)	1.21E5	1.89E3(7E2)
15	5.99E-3(6E-3)	200.0(200.0)	8.62E4	1.35E3(5E2)
16	6.99E-2(7E-2)	200.1(200.0)	6.04E4	9.24E2(3.5E2)
17	.35(.35)	200.4(200.0)	5.17E5	7.18E3(3E2)
18	1.238(2.0)	201.2(200.0)	172.4	1.62(15)
19	2.93(20.0)	202.9(200.0)	172.4	1.72(9)
20	3.09(100.0)	203.1(200.0)	172.4	3.19E-2(10)

Source: Wahlberg and Fishman (1962)
(Quantities in parentheses are the experimentally measured values).

possible explanation is the incomplete separation of clay particles from the solution. The presence of adsorbed Cs⁺ on the clay particles caused the measured value of K_d to be lower than the true value.

Although these experiments dealt with binary exchange, the results are useful in the simulation of ternary and multicomponent exchange processes. Dranoff and Lapidus (1957) showed that data from binary exchange experiments could be extrapolated to predict the behaviour of ternary or

even higher order systems.

Having developed an algorithm for equilibrium ion exchange, it remains to describe the operation with the MOC. Because of the two steps in the MOC, advection of reference particles and convection due to dispersion, the aqueous phase must be re-equilibrated after each step or twice within each time step. Thus my approach, while conceptually included in the family of "two-step" procedures, actually involves four steps.

The exchange calculation is applied to each cell within the two-dimensional domain. Unequilibrated concentrations (cell means) of ions in solution and on the exchanger together with other parameters required for the calculation, such as bulk density, porosity, CEC and selectivity quotients, are passed to subroutine CATEX which carries out the iterative procedure. The equilibrium concentrations returned from CATEX constitute the new mean values for concentration in the cell and are applied as well to adjust the concentrations carried by the moving reference particles.

A flow chart of the complete MOC-exchange model is given in Appendix 4 together with a listing of the code. A sample data set is also included in Appendix 4. At present the code is written to simulate ion exchange with three ions on any number of exchangers.

TABLE 15. RESULTS OF SIMULATION OF EXCHANGE ADSORPTION OF CESIUM ON ILLITE AND KAOLINITE

Exchangers:

Na- Kaolinite No.4, C.E.C.= 10meq/100g. (Runs 21 to 26)

Na- Illite No.35, C.E.C.= 15meq/100g. (Runs 27 to 30)

Exchanging Cations: Cs-Na

Simul- ation Run	Conc. of Cs, mmol	Conc. of Na, mmol	K' (Cs)	K _d
21	9.99E-6(1E-7)	2.0(2.0)	7E3	9.2E2(3.5E2)
22	2.99E-4(3E-4)	2.0(2.0)	8E3	1.05E3(4E2)
23	9.96E-6(1E-7)	10.0(10.0)	1E4	2.63E2(1E2)
24	1.99E-6(2E-6)	20.0(20.0)	3E4	3.95E2(1.5E2)
25	9.81E-6(1E-7)	200.0(200.0)	4E4	52.6(20)
26	.962(.01)	200.0(200.0)	2E4	25.3(10)
27	9.99E-6(1E-7)	2.15(2.00)	1.07E6	1.45E5(8E4)
28	1.00E5(1E5)	20.14(20.00)	1.33E6	1.93E4(1E4)
29	4.99E-3(5E-3)	2.15(2.00)	6.68E4	8.86E3(5E3)
30	2.00E-4(2E-4)	200.1(200.0)	3.33E6	4.83E3(2.5E3)

Source: Wahlberg and Fishman (1962)

(Quantities in parentheses are the experimentally measured values)

3.2.5 Validation of the MOC Code

The validation step in the development of a computer code is designed to demonstrate that the code is operating as implemented to produce accurate numerical solutions. In this study, a three phase validation procedure is utilized. Phase 1 involves the validation of the basic MOC model; the ion exchange routine is checked in Phase 2; and, in Phase 3 the complete MOC- ion exchange code is tested.

The MOC model is verified for a one-dimensional problem by comparing the time variation in concentration calculated numerically with the analytical solution coded by Cleary and Ungs (1978). The one-dimensional flow and transport, which develops in the domain shown in Figure 19A,

is determined by the boundary conditions and the indicated velocity and dispersion coefficients. The comparison of the two solutions for this problem is shown in Figure 19B. In general, the MOC solution compares very well with the analytical solution. Minor deviations are apparent where the slope of the concentration- time curve changes markedly.

The model is verified also in two dimensions by comparison with the analytical solution to the problem of two- dimensional, transient dispersion of a solute in steady, one- dimensional flow through an isotropic, porous medium obtained by Bruch and Street (1967). A complete derivation of the solution is given by Bruch and Street (1967) and details of the experiments are described by Bruch (1970). The run parameters in my simulation are estimated with the data from these two papers. Figures 20A and B show the simulation of a dispersion experiment described by Bruch and Street (1967). The MOC solution reproduces the pattern of dispersion reasonably well although some discrepancy is apparent at the fringes of the plume of tracer. As will become apparent later, this discrepancy develops because an optimum combination of space ($\Delta x, \Delta z$) and time (Δt) steps is not obtained.

Analytical solutions to the advection- dispersion transport problem have been determined by Shamir and Harleman (1967) for the two- layer situation in two dimensions. The flow field is parallel to the stratification and is in steady state. Additionally, compatibility

conditions require the concentration and fluxes of the solute to be equal at the interface between layers. The solution of Shamir and Harleman (1967) is derived for the case in which the distribution of the solute within the flow domain is in steady state, so that the results are presented as $C(x,y)$ at the cross-section $x = x_1$. I programmed the equations for the concentration distribution in the first and second layers given by Shamir and Harleman (1967) with the properties of the Milk River Shale and Milk River Sandstone in the lower and upper layers respectively. It is necessary to run the MOC solution over a long period of time to achieve a steady state solution and obtain an acceptable match.

The accuracy of the complete transport model is validated through the use of a one-dimensional, analytical solution. As Bear (1972, 1979) and Freeze and Cherry (1979) show, it is possible to build simple binary exchange into an analytical solution by dividing the velocity and dispersion coefficients by a retardation factor, R . This factor is related to the parameters of ion exchange by

$$R = 1 + (\rho/n) \cdot K_d \quad (63)$$

Freeze and Cherry (1979)

where ρ is the bulk density of the porous medium. Using this theory, it is possible to set up a problem of binary exchange that can be solved both analytically and numerically. There are slight differences in the two approaches because of the simplifying assumptions necessary

in developing the analytical solution. However, by keeping the exchanging ion, i.e. T^+ , at trace concentration relative to the counter ion, these differences become negligible.

The parameters for both of these simulations are depicted in Figures 21A and B together with the appropriate solutions. In general, there is fair agreement between the two sets of results. However, the numerical solution in the zone of dispersion overestimates the concentration at less than the 0.5 value of C/C_0 and underestimates it at concentrations greater than this value. This behaviour in the numerical solution is termed 'numerical dispersion' and is caused by the numerical approximation technique which generates physical dispersion in excess of that determined by the dispersion coefficient.

To investigate this problem in more detail several more simulation trials are carried out in which only the size of the time step and grid blocks are varied. The results shown in Figure 22 compare the various numerical solutions with the analytical solution at 2923.2 days. They show that as either the size of the time step or the grid size decreases the numerical solution becomes more accurate. Because the MOC clearly does not suffer from numerical dispersion, it is most likely that this problem developed as a consequence of adding the ion exchange routine. A possible explanation is that the time and space averaging inherent in the ion exchange calculation produces small errors especially where

concentrations are changing rapidly. However, these small errors are not cumulative with the time advance of the solution.

The interrelationships between R , K_d and the concentration of a competing cation is demonstrated by using the ion exchange and one-dimensional transport models in tandem. The latter model is coupled to the velocity and dispersion terms of MOC by means of the retardation factor, R . The Cleary and Ungs (1978) solution is used as the transport model with the ion exchange data from Wahlberg and Fishman (1962). Cs^+ is chosen as the trace ion because of its importance in contaminant hydrogeology. Also, the exchange of Cs^+ on various materials has been studied exhaustively and its ion exchange behaviour is well known under a wide variety of conditions, (Faucher and Thomas, 1954; Amphlett and McDonald, 1956, 1958; Wahlberg and Fishman, 1962; Coleman et al, 1963; Coleman and LeRoux, 1965; Sawhney, 1964, 1965, 1966, 1970). The influence of the concentration of the competing cation in most cases is seen to outweigh the difference in the CEC of the clay mineral exchanger and the varying magnitude of K_d for adsorption on pure clays.

The relative concentration, C/C_0 , at various distances within a simulated clay core is shown on Figure 23B for various combinations of the parameters listed in Figure 23A. The most rapid transport occurs in Runs 20 and 26 in which the concentration of Na^+ is very high. Other runs, for

example 27 as compared with 21 and 1, and 2 as compared with 22, demonstrate the effect of selectivity coefficient and CEC of the different clay minerals on similar concentration ratios of Na^+ to Cs^+ . Thus, among these latter groups there is greater ion retardation of cesium in media consisting of montmorillonite than on illite or kaolinite.

3.3 Simulation of Mass Transport with the MOC Model

3.3.1 One-Dimensional Homogeneous Media

Mass transport in a steady, one-dimensional flow domain is modelled using the MOC on some of the simulated granular media described previously in Chapter 2. Initially, the media 8B, 9B, 11B and 12B are selected from those listed in Appendix Table A3.2.1 to demonstrate the effects of the mean grain size and sorting of homogeneous, isotropic, silty sands on mass transport within such sediments. Next, mass transport is simulated in 11B and 12B with each of kaolinite, illite and montmorillonite and then varying proportions of all three minerals in the clay fraction. The influence of the clay minerals upon the rate of movement of the tracer solute can be examined by comparing the distance travelled in the same media when no clay is present.

The distance travelled by a solute in steady, unidirectional flow is related to the mass flux of fluid through the flow domain. Hence it is a function of the groundwater flow velocity which is governed by the

permeability of the porous medium. For all the simulations, a hydraulic gradient of unity is assumed and the velocity is calculated from the equation presented by Harleman et al. (1963). Use of a unit gradient resulted in high velocities for the more coarse grained sediments, but in all cases the Reynolds Number of the flow was less than the upper limit for laminar flow as stated by Todd (1980). These velocities are listed in Table 16.

In those cases of simulated media which contain clay minerals, the travel distance of the solute is decreased relative to the velocity of the convecting fluid due to ion exchange. The selectivity coefficients for each trace ion T_1 and T_2 are set to .01 and .02 respectively for an examination of this effect between the ions. These values are selected arbitrarily to examine the effects of the relative retardation and do not represent physically realistic values for cations of interest. The influence of the mean grain size and clay mineralogy in reducing the travel time of the trace constituents in the solute is clearly seen on Figures 24A and B, 25, 26, 27 and 28. The size of the time step, Δt , in the MOC solution is constrained by the magnitude of the flow velocity, so that smaller time steps are required at high velocities to ensure stability. Hence it is not feasible to run the simulations to a common total time. Thus, to provide a basis for comparison of the transport properties of all of the media, the concept of "relative velocity" is developed. The

TABLE 16. FLUID VELOCITY FOR ONE-DIMENSIONAL RUNS ON SIMULATED MEDIA

Medium	Clay Type	Fluid Velocity (m/d)
8B	None	3.900
9B	None	1.280
11B	None	0.270
11B	Kaol.	0.210
11B	Illite	0.190
11B	Montmor.	0.160
11B	Mixt. 1	0.201
11B	Mixt. 4	0.186
11B	Mixt. 5	0.191
11B	Mixt. 7	0.168
12B	None	0.027
12B	Kaol.	0.020
12B	Illite	0.013
12B	Montmor.	0.005
12B	Mixt. 1	0.016
12B	Mixt. 4	0.010
12B	Mixt. 5	0.012
12B	Mixt. 7	0.006

relative velocity is defined as the time in years required for 50% of the relative concentration, C/C_0 , to travel 100 metres from the source. The relative velocities of the trace constituents T_1 and T_2 are tabulated in Table 17.

The influence of mean grain size upon mass transport without ion exchange, i.e. in the absence of clay minerals, is demonstrated by Figure 24A and B. In this Figure the relatively rapid transport of the solute is related to the high flow velocity consequent upon the high permeability of media 8B and 9B. The much lower permeability values of media 11B and 12B are reflected in their lower relative velocity. The relatively steep front results from the low values of dispersivity used in the simulations.

TABLE 17. RELATIVE VELOCITY, RV, OF TRACE IONS T_1 AND T_2 :
ONE-DIMENSIONAL RUNS IN SIMULATED MEDIA

Medium	RV of T_1 (years)	RV of T_2 (years)
8B-No Clay	0.104	0.104
9B-No Clay	0.159	0.159
11B-No Clay	1.026	1.026
11B-Kaol.	1.364	1.436
11B-Illite	1.627	1.776
11B-Montmor.	2.411	3.177
11B-Mixt. 1	2.213	2.250
11B-Mixt. 4	1.500	1.525
11B-Mixt. 5	1.824	1.902
11B-Mixt. 7	1.776	1.929
12B-No Clay	9.001	9.001
12B-Kaol.	20.65	27.96
12B-Illite	48.61	75.24
12B-Montmor.	350.9	632.9
12B-Mixt. 1	78.99	83.13
12B-Mixt. 4	20.79	21.50
12B-Mixt. 5	41.58	43.90
12B-Mixt. 7	34.35	39.49

The effect of adding 10% of single clays to the media 11B and 12B are graphed in Figures 25 and 26 respectively. In each case the retardation of the solute increases from kaolinite through illite to montmorillonite, and the relative retardation compared to the case of no clay is much greater for Run 12B than for Run 11B. These effects result from the large CEC of montmorillonite vis-à-vis illite kaolinite and to the lower velocity and greater dispersion in Run 12B.

Similar effects are noted in Figures 27 and 28 in which the retardation due to mixtures of clays is plotted respectively for Runs 11B and 12B. Inspection of the Figures conjointly with Table 12 shows that Mixture 1, which contains the greatest amount of kaolinite, results in the

least retardation. Mixture 7, which contains the greatest amount of montmorillonite, shows the greatest retardation. The remaining mixtures, Mixtures 4 and 5, show similar relative velocities, indicating that mass proportional effect of a single clay, illite, is similar to that of a mixture of all three clay minerals.

3.3.2 Two-dimensional Layered Media

As a preliminary step towards the simulation of mass transport through actual geological sections the performance of the MOC model on layered media composed of some of the artificial sediments of Chapter 2 is studied. These stratified media are constructed by adding successive, uniformly thick, homogeneous, isotropic layers to form two-layered, three-layered and four-layered porous media respectively. The transverse dispersivity, α_2 , is set to one tenth of the longitudinal dispersivity, α_1 . The overall objective is similar to that for the one-dimensional and two-dimensional homogeneous media, namely to demonstrate the effects of grain size and mineralogy on the transport attributes of the sediments. A further objective is to demonstrate that the MOC code is capable of producing a realistic simulation of mass transport within the individual layers.

The effect of the magnitude of the contrast in the properties of each layer on the stability of the MOC solution is examined in the light of the compatibility

requirements at the interface between adjacent layers. It is possible that the solution might become unstable for certain values of the velocity in each layer, because the procedure averages concentrations at the nodes across the boundary. This is found to be the case, and suitable adjustments of the time step are required in layered systems to ensure stability and accuracy of the solution in the region of the boundary. Figure 29 depicts the relative concentration profiles within layered media consisting of 8B/11B and 8B/12B respectively, resulting from the continuous injection of tracer into both layers at $x = 0$. The combination of time and space steps proved to be stable over a velocity contrast of up to two orders of magnitude between the layers.

The shape and position of the relative concentration front at the interface between the media are controlled by the magnitude of the contrast between the properties of each medium, due to the averaging of velocities at the interlayer nodes of the grid. The physical situation in which there would be lateral dispersion of solute from the higher velocity layer to the lower velocity layer because of the more rapid advance of the solute in the former, is simulated by the numerical procedure.

The advance of a plume of solute in a three-layered medium is shown in Figures 30 and 31. In both instances the effect of the inter-layer boundary zones on the shape of the plume is readily apparent. The increased retardation of the solute in 11B and 12B as compared to 8B is due to the

lower fluid velocity in those layers consequent upon their lower permeability. However, the increased retardation in the various clay runs of 12B reflects the greater CEC of illite and montmorillonite vis-à-vis that of kaolinite. In this case only the concentration of the trace constituent with the lesser affinity for the exchanger is plotted, as the relative concentration contours for the other ion would show a similar but spatially displaced pattern.

3.3.3 Layered Geological Strata

The simplest idealization of an actual sedimentary sequence is that of the perfectly stratified aquifer in which there is unidirectional, steady flow parallel to the strata. Two-dimensional mass transport in a hydrogeological system of this type may be simulated with MOC both for the case of a conservative solute and for one in which the concentration of the solute is modified by ion-exchange. If the hydraulic and transport properties of the aquifer are not known a priori, it has been shown that estimates may be calculated with GENPAR1 or GENPAR2 as appropriate.

A problem which has been discussed briefly in Chapter 2 is that of the increase in the dispersion coefficient when the flow domain is scaled up from the laboratory column to the field. This problem is approached in the MOC model by calculating the longitudinal and transverse dispersion coefficients as a function of the average velocity of particles in a grid cell. However, because GENPAR1 and

GENPAR2 do not account for variations in velocity at the macroscopic scale, values of the dispersion length will tend towards those of the laboratory column scale.

Klotz et al. (1980) showed experimentally that dispersion lengths defined on laboratory columns over the range of material and fluid velocities listed in Appendix 2 could be applied in the field over a distance of up to about 50 metres. The effect of using laboratory scale dispersion lengths over the distances involved would be to underestimate the distance travelled by the leading edge of the plume, whereas the position of the 50% relative concentration, C/C_0 , would not be affected significantly. For example, in the case of one-dimensional transport within the simulated sediments, an increase in the value of dispersivity over four orders of magnitude did not affect significantly the position of the 50% relative concentration. The positions of the leading and trailing edges of the plume were altered by less than ten percent.

The utility of the MOC model in simulating mass transport under the conditions described in the previous paragraph is shown by applying the model to various real geological sections. In these scenarios the input parameters for the MOC model are determined from the lithology and mineralogy of the formation by means of GENPAR1 and GENPAR2. Starting with a simple two-layered situation, exemplified by the Milk River Sandstone of Southern Alberta, multilayered sections from the Oxnard aquitard of California

and the Muddy Sandstone of Montana and Wyoming are used to demonstrate the simulation of movement of hypothetical conservative and reactive solutes in groundwater.

Example 1 - Milk River Sandstone of Southern Alberta.

The application of GENPAR1, GENPAR2 and MOC to an idealized, two-layered system is demonstrated for the Milk River Sandstone of Southern Alberta. The bulk properties of this formation have been described earlier in Chapter 3 and in Appendix 1. The "typical" Milk River Sandstone according to Meyboom (1960) in the outcrop area of the formation in the western half of Sec.16, Tp.2, R.14 is a sequence of sandstone and underlying shale which is continuous for several hundreds of metres. Evans (1931) indicates that the Lower Milk River Formation, now termed the Virgelle Member (Meijer Drees and Myhr, 1981), varies in thickness between 23 and 32 metres. The Virgelle Member appears to represent the "typical" Milk River Sandstone of Meyboom (1960).

The formation is idealized for the simulations into a rectangular flow domain with the dimensions, boundary and initial conditions shown on Figure 32A. The effects of varying the initial concentration conditions on the movement of reactive solutes are clearly shown by the Figures. The MOC model is run with a time step of 12.18 days and spatial increments of 10 metres. This combination of parameters is able to demonstrate the influence of the boundary between the layers on the distribution of the reactive solute.

The boundary and initial conditions for the application of the solution of Shamir and Harleman (1967) for mass transport of a solute in a two-layered, steady-state flow domain have been described previously. Figure 32A depicts the various initial and starting conditions for the analytical and numerical solutions in the idealized Milk River Formation. For consistency with the initial conditions specified by Shamir and Harleman (1967), the analytical runs (2) and (3) assume that the input concentration across $x = 0$ is a function of the y coordinate. With the notation that the concentration in Layer 1 is C_1 and that in Layer 2 it is C_2 , then the initial and equivalent starting conditions for analytical runs (2) and (3) are

$$C_1, C_2 = C_0 \quad -y \leq 0 \leq y \quad (\text{numerical run 1})$$

$$C_1 = C_0 \quad y \leq 0$$

$$C_2 = 0 \quad y > 0 \quad (\text{numerical run 2})$$

$$C_1 = C_0 \quad y < B$$

$$C_1 = 0 \quad 0 > y \geq B$$

$$C_2 = 0 \quad y > 0 \quad (\text{numerical and analytical runs 3})$$

In the simulation, the Milk River Shale of Meyboom (1960) is represented by Layer 1 and the Milk River Sandstone by Layer 2. The properties of the layers are determined from GENPAR1, and are listed in Appendix Table A3.2.5.

The results of the numerical runs (1) and (2) are shown in Figures 32B and 32C. When the solute is input uniformly

across both layers, it travels more rapidly in the Milk River Sandstone, as expected, but also there is considerable diffusion of solute across the boundary between the layers, leading to a more rapid movement in that region than would be the case for a homogeneous medium. Numerical run (2) shows that although the overall distance travelled by the solute in the Milk River Shale is similar to Run (1) after 2.7 years, the interlayer transfer of solute is greatly reduced. The phenomenon is duplicated by the analytical runs (2) and (3), in which the steady state relative concentration profile, graphed in Figure 32D, is calculated. This Figure shows that for the initial and starting conditions of run (2), the steady state plume would be confined mostly to the Milk River Shale, as very little interlayer transfer of solute would result.

Example 2 - Oxnard Aquitard Section, California.

The second series of simulations is based on parameters descriptive of the aquitard section between the Oxnard and Mugu aquifers in the Oxnard plain of Ventura County, California. The section represents a well-documented vertical section of some 40 metres of low permeability silt and clayey silt with a single layer of high permeability, gravelly sand. Although the section is relatively homogeneous in mineralogy and lithology, it displays considerable variation in the permeability. Hence it would be a severe test of the ability of the MOC model to simulate transport in a multi-layered situation with considerable

variation in velocity between the layers. However, to maintain the condition of flow parallel to the layers the aquifers are replaced by fictional aquicludes. Data from borehole cores published by Mitchell et al. (1971) are used to determine the stratigraphy of the Oxnard section and to calculate the properties of the individual layers.

The porosity and permeability of each layer are estimated for each layer by means of GENPAR1 using the grain size distribution plots in Mitchell et al. (1971). It is necessary to use the graphical extrapolation technique described in Appendix 1.2 in order to estimate the lower bound of the finest sized fractions for the determination of permeability and porosity with (12) and (2) respectively. The longitudinal dispersivity of the material is estimated from (31). The fractional mineral content of the silt- and clay- sized fractions was averaged to be: montmorillonite (.64); kaolinite (.19); vermiculite (.03); illite (.04); quartz (.10). The sand- sized fraction is assumed to consist entirely of quartz. The density, specific surface and CEC of these minerals are taken from published tables.

The results of the parameter estimates are compared to measured values of porosity, permeability, and CEC in Figure 33. In these soft, easily deformable sediments the in-situ porosity, stated as the initial void ratio by Mitchell et al. (1971), is related strongly to the structural fabric of the sediment and to the overburden pressure. Thus, the size and other related parameters of the disaggregated grains

cannot strictly predict the porosity but will provide an estimate at a condition of zero effective stress. Nevertheless I use the predicted values because actual void ratios are available for only four of the sampled intervals.

The permeability pattern is reproduced broadly, except for the lowermost layer which consists of a stiff, fissured clay, to which the assumptions of GENPAR1 are not applicable. Exact duplication of the CEC proved to be impossible, although the trend of decrease with depth is matched. Mitchell et al. (1971) indicate that the concentration of vermiculite in silty sediments of the Oxnard Plain is difficult to quantify. In this event, the high unit CEC of vermiculite could affect the overall CEC of the material if the averaged concentration of the mineral is overestimated.

Table 18 summarizes the parameters used in the MOC simulation runs. Because the vertical section of the aquitard is relatively homogeneous lithologically the properties measured on or simulated from each interval sampled in the core are assumed to vary smoothly across the clayey silt. Consequently, the section can be idealized into seven homogeneous, isotropic layers of equal thickness, overlain by a single, similarly idealized layer of gravelly sand. The results of the simulation of this section with the MOC model are presented in Figures 34 and 35. The influence of the high permeability of layer 1 on the movement of the solute is very clearly shown by the Figures. In this case

TABLE 18. PARAMETERS FOR THE SIMULATION OF MASS TRANSPORT IN THE OXNARD AQUITARD SECTION

Layer	Porosity	Bulk Density (g/cm ³)	Fluid Velocity (m/d)	Dispersivity (cm)	CEC (meq/100g)
1	.283	1.90	3.55	3.1E-2	1.85
2	.377	1.64	.001	1.4E-3	43.56
3	.448	1.45	5E-4	8.2E-4	55.24
4	.518	1.26	.002	2.2E-4	58.31
5	.512	1.28	.004	1.8E-3	55.24
6	.436	1.48	.001	1.1E-3	57.69
7	.287	1.88	3.4E-5	2.4E-3	45.36
8	.423	1.52	.006	1.1E-3	44.74

the retardation of the solute in layers 2 through 8 is a result of the combined effect of the much lower permeability and greater CEC of those layers. This latter effect is diagrammed in Figure 35A and B, in which the ratio of the velocity of the conservative compared to the reactive ions in layers 5 and 8 is 3.1 and 4.8 respectively.

Figures 35A and 35B provide some more detail on the transport of mass within the seven layers of the section below the high permeability layer 1. It was necessary to run the simulation for 9600 days in order to obtain a measurable profile. The effect of lateral dispersion in spreading the solute from layers of higher to lower permeability, for example from 4/5 to 6 and 3, and from 8 to 7 respectively, is clearly shown in both Figures. Nevertheless, the overall pattern is one of transport of the plume of solute within individual layers in the direction of groundwater flow at a rate which is proportional to the permeability of each layer. This pattern has been observed in field studies of

artificial recharge in stratified aquifers, (Mercado, 1967), and of contaminant plumes from landfill sites in unconsolidated sediments, (Kimmel and Braids, 1975).

Example 3 - Muddy Sandstone of Montana and Wyoming.

The Lower Cretaceous Muddy Sandstone in the Powder River Basin of northeastern Wyoming and southeastern Montana consists of interbedded sandstone, siltstone and shale some 50 metres in thickness, (Almon and Davies, 1979). Berg and Davies (1968) and Almon and Davies (1979) from examination of well logs and drill cores are able to show that there is an interrelated zonation of sedimentology and diagenesis within the formation. Almon and Davies (1979) divided the formation into six time- sequential sedimentologic zones as follows:

- (a) 1 and 2: barrier and deltaic sedimentary environments;
- (b) 3 and 4: delta-destructive barrier sedimentary environments;
- (c) 5 and 6: fluvio-deltaic sedimentary environments.

These sedimentologic zones are grouped into three diagenetic zones, each of which contains a distinctive mineral suite, as shown in Table 19. The mineralogy is further subdivided into:

- (a) *stables*: detrital quartz;
- (b) *unstables*: feldspar, mica, quartz and rock fragments;
- (c) *matrix*: authigenic quartz, illite, chlorite, kaolinite and montmorillonite.

Almon and Davies (1979) include monocrystalline quartz and

TABLE 19. SEDIMENTOLOGIC AND DIAGENETIC ZONES WITHIN THE MUDDY FORMATION *

Sedimentologic Zone	Diagenetic Zone	Mineralogy
1,2	A	kaolinite, quartz
3,4	B	kaolinite + illite-smectite + tr. of chlorite
5,6	C	kaolinite + high Fe-chlorite + Fe-illite/smectite

*Source:
Almon &
Davies (1979)

polycrystalline quartz with five or less crystals per grain in the stable fraction; polycrystalline quartz with more than five crystals per grain are assigned to the unstable fraction. Matrix is defined as material with grain size of less than 20μ . Lithologically the sediments may be classified as lithic to quartz arenites.

The data presented by Berg and Davies (1968) and Almon and Davies (1979) are sufficiently comprehensive that estimates of the requisite parameters for modelling mass transport in borehole sections typical of diagenetic zones A and B could be made. These simulations enable comparisons between transport in high porosity and high permeability sandstones to be made on the basis of their detrital and authigenic mineralogy. Mass transport in Zone C is not simulated because its extremely high permeability is outside the range of validity of the correlations between this

quantity and dispersivity for sandstones developed in Chapter 2. Further, the mineralogy is sufficiently similar to that of Zone B that significant differences in the mass transport characteristics are unlikely to be achieved.

Berg and Davies (1968) present a graph of the permeability measured in the laboratory versus the mean size of quartz grains from cores taken in the Bell Creek oilfield in Montana. A modified version of this graph is shown in Figure 36A. This relationship is applied to the determination of the permeability of the sections penetrated by boreholes Bell Creek Boekel 21 - 14, NE NW 14 (representative of Zone A2), and Recluse Apache No.1 State Geronimo NW SE 16 - 56N - 74W (representative of Zone B4). Electric logs of the Muddy Sandstone interval in these boreholes are shown in Figures 36B and 36C; the position of the cored section is also shown on these Figures. Table 20 lists the mean grain size and composition of the stable, unstable and matrix mineral fractions of each core from positions 1 through 10 and 1 through 12 respectively of Zones A2 and B4. Table 21 compares the permeability of each section as computed from the Berg and Davies (1968) relationship to that computed with GENPAR2 using the mineral composition of each core position. These data are listed in Table 22 and are calculated from mineral concentrations given by Almon and Davies (1979). The values of porosity used in GENPAR2 to obtain the estimates of permeability are derived from relationships given by Carothers (1968).

TABLE 20. MEAN GRAIN SIZE AND FRACTIONAL CONCENTRATION OF STABLE, UNSTABLE AND MATRIX MINERALS IN MUDDY SANDSTONE CORES

Core Position	Mean Grain Size(cm)	Stable	Unstable	Matrix

Zone A2				
1	.012	.84	.08	.08
2	.013	.85	.09	.06
3	.014	.79	.15	.06
4	.020	.95	.05	.00
5	.021	.96	.04	.00
6	.020	.90	.10	.00
7	.019	.89	.11	.00
8	.019	.91	.09	.00
9	.016	.79	.05	.16
10	.004	.45	.06	.49
Zone B4				
1	.018	.58	.07	.35
2	.015	.65	.02	.33
3	.016	.87	.05	.08
4	.015	.62	.09	.29
5	.010	.67	.02	.31
6	.018	.95	.05	.00
7	.015	.55	.20	.25
8	.015	.90	.00	.10
9	.014	.95	.00	.05
10	.018	.98	.00	.02
11	.021	.94	.00	.06
12	.026	.95	.00	.05

The core descriptions of Berg and Davies (1968) and Almon and Davies (1979) do not include porosity measurements, but estimates of this quantity are obtained from

$$F^{1/2} = 7.0E+8/k$$

and,

$$F = 1.38/n^{1/2}$$

where F is the formation factor, n is the porosity and k is the permeability in millidarcies. The relationship between F and n is derived by Carothers (1968) with measurements on

cores from Cretaceous sandstones in the United States, while that between F and k is derived for consolidated rocks of all geological ages. Berg and Davies (1968) note that the maximum porosity observed in core from Zone A2 is 33%, so the porosities predicted with the Carothers (1968) relationship are preferred to those predicted by (19) as programmed in GENPAR2. These latter values are systematically lower, suggesting that the values of G and x for sandstones in Table 6 may not be appropriate in the case of the Muddy Formation.

Having estimated the porosity and permeability of sections A2 and B4, the dispersivity and fluid velocity are calculated using the standard procedures. However, because of the high values of permeability it is necessary to reduce the head gradient from 1 to .01 in order to obtain fluid velocities within the laminar flow range in the most permeable layers. Finally the CEC of each of the unstable and matrix fractions is estimated using GENPAR2. All these parameters are listed in Table 23. Values of CEC set to .001 actually indicate negligible quantities, but the numerical procedure in MOC requires a small, non-zero value for accurate results.

The number of layers in each simulated section is determined by the number of core positions. As in the Oxnard case, the vertical variation in core properties is sufficiently smooth to postulate layers of equal thickness. Inspection of the electric log of Bell Creek Boekel 21 - 14,

TABLE 21. PREDICTED PERMEABILITY, FORMATION FACTOR AND POROSITY, MUDDY SANDSTONE, ZONES A2 AND B4

Core Position	¹ Permeability (cm ²)	² Permeability (cm ²)	³ F	² F	³ Porosity
Zone A2					
1	2.96E-9	2.99E-9	43.37	35.10	.13
2	5.40E-9	4.52E-9	37.90	27.40	.15
3	1.04E-8	2.43E-8	32.85	24.50	.16
4	6.91E-7	1.74E-6	12.92	9.29	.28
5	1.38E-6	4.35E-6	11.07	7.78	.31
6	6.91E-7	6.32E-6	12.92	9.29	.28
7	4.94E-7	1.91E-7	13.92	11.30	.25
8	4.94E-7	3.46E-7	13.92	11.30	.25
9	9.41E-8	9.43E-8	23.22	19.98	.18
10	4.94E-11	5.79E-11	107.76	81.35	.08
Zone B4					
1	2.27E-7	1.63E-7	16.54	14.11	.22
2	2.66E-8	5.53E-8	26.62	22.06	.17
3	4.94E-8	6.31E-8	23.32	19.80	.18
4	2.66E-8	9.45E-8	26.62	22.06	.17
5	4.83E-10	3.67E-10	64.91	55.28	.10
6	2.27E-7	5.66E-8	16.54	14.11	.22
7	2.66E-8	7.73E-8	26.62	22.06	.17
8	2.66E-8	6.05E-8	26.62	22.06	.17
9	1.04E-8	1.26E-8	32.85	24.50	.16
10	2.27E-7	6.70E-7	16.54	14.11	.22
11	5.12E-6	1.38E-6	11.07	7.78	.31
12	2.48E-5	1.97E-5	6.13	5.22	.39

¹Predicted from Berg and Davies (1968) relationship;

²Predicted with GENPAR2;

³Predicted from Carothers (1968) relationship.

NE NW 14 (Zone A2) suggests that there are no prominent shale breaks within the cored section so that layers 1 through 10 could be considered to be conterminous. However, the log of Recluse Apache No. 1 State Geronimo NW SE 16 - 56N - 74W shows that a thick shale break occurs between core positions 7 and 8. Thus, layers 1 to 7 and layers 8 to 12 were modelled as distinct groups. Nevertheless, the location of this borehole within a delta- destructive, barrier facies implies that the shale break will likely be less continuous

than the sand bodies, (Davies et al, 1971; LeBlanc 1977a, 1977b; Sneider et al, 1978), so that the assumption of a uniformly layered sequence as shown in Figures 37 and 38 is a reasonable one. Barrier sand bodies are characteristically elongated along the regional strike and are hydraulically continuous in both the strike and dip directions, (LeBlanc, 1972; 1977a). An isopach map of the gross thickness of the Muddy Sandstone in the Bell Creek oilfield shows the sandbodies to be elongated parallel to the regional strike over a distance of tens of kilometres with an average width of 1 to 2 kilometres in the dip direction. Thus, the dimensions of the domain shown in Figure 38 appear to be realistic from the geologic standpoint.

Variations in the fluid velocity which are governed by the permeability of the layers are the primary controls on mass transport within the Muddy Sandstone. One problem with the simulation of a multi-layered system is the difficulty of achieving an optimum combination of time and space increments to satisfy the wide range of variation in velocity. This problem is handled in the MOC code by substituting the mean velocity within each layer for the velocity averaged across the layer boundary. The dispersion in the region of the boundary is reduced slightly, but the general spatial pattern of the plume is not unduly affected.

The results of the simulation of the Muddy Sandstone illustrate the effect of large differences in permeability, caused primarily by differences in mean grain size, on the

TABLE 22. FRACTIONAL MINERAL COMPOSITION OF MUDDY SANDSTONE ZONES A2 AND B4

CP	Qd	Fs	Mi	RF	Qa	It	Cl	Kl	Mt
Zone A2									
1	.840	.020	.040	.040	.050	.000	.000	.020	.020
2	.850	.020	.020	.050	.037	.000	.000	.015	.008
3	.790	.037	.037	.076	.037	.000	.000	.015	.008
4	.950	.012	.012	.026	.000	.000	.000	.000	.000
5	.960	.010	.010	.020	.000	.000	.000	.000	.000
6	.900	.020	.020	.060	.000	.000	.000	.000	.000
7	.890	.027	.027	.056	.000	.000	.000	.000	.000
8	.910	.020	.020	.050	.000	.000	.000	.000	.000
9	.790	.013	.013	.024	.100	.000	.000	.040	.020
10	.450	.015	.015	.030	.306	.000	.000	.123	.061
Zone B4									
1	.580	.009	.052	.009	.228	.012	.017	.070	.023
2	.650	.003	.014	.003	.214	.011	.016	.067	.022
3	.870	.007	.036	.007	.052	.003	.004	.016	.005
4	.620	.012	.066	.012	.189	.009	.014	.058	.020
5	.670	.003	.014	.003	.202	.010	.015	.062	.021
6	.950	.007	.036	.007	.000	.000	.000	.000	.000
7	.550	.030	.140	.030	.162	.008	.012	.050	.018
8	.900	.000	.000	.000	.064	.004	.006	.020	.006
9	.950	.000	.000	.000	.032	.002	.003	.010	.003
10	.980	.000	.000	.000	.013	.001	.001	.004	.001
11	.940	.000	.000	.000	.039	.003	.003	.012	.003
12	.950	.000	.000	.000	.032	.002	.003	.010	.003

CP = core position; Qd = detrital quartz; Qa = authigenic quartz;
 Fs = feldspar; Mi = mica; RF = rock fragments; It = Illite;
 Cl = chlorite; Kl = kaolinite; Mt = Montmorillonite.

spreading pattern of a plume of solute from a source input across the layers at $x = 0$. In this case the low CEC of the various layers meant that the influence of the authigenic mineralogy on the overall spread of the plume is minor. However, the combined effect of small grain size and a high CEC could result in strong retardation of the solute. Nevertheless, inspection of Figure 37 elicits that for instance, in Layer 10 of Zone A2 with a mean grain size of .004 cm and 49% of matrix minerals, the movement of the

solute is not significantly greater than in Layers 1 and 2 in which the mean grain size and matrix mineral component are .012 cm and .013 cm and 8% and 6% respectively. On the other hand, there is very much greater transport in Layers 4 and 5 in which the mean grain size is .020 cm and .021 cm, and in which there are no matrix minerals, resulting in a negligible CEC.

Similar patterns of solute movement are observed in Section B4 of the Muddy Sandstone. The large mean grain size in Layers 11 and 12 outweigh the effects of the moderate CEC of these layers to promote a very large transport distance. However, in Layers 1 to 7, the differences in the CEC caused by the wide variation in the concentration of authigenic minerals in the matrix of the rock impose significant differences on the transport characteristics of each layer. Thus, transport is most rapid within Layer 6 in which the CEC is negligible, although its mean grain size is not significantly different from the rest of that group of layers. In general, mass transport within the Muddy Sandstone appears to be governed primarily by the original sedimentology of the formation; the diagenetically created suite of authigenic pore minerals can impose locally significant variations on this pattern of mass transport.

TABLE 23. PARAMETERS FOR THE SIMULATION OF MASS TRANSPORT IN LAYERS OF MUDDY SANDSTONE, ZONES A2 AND B4

Layer	Dispers- ivity (cm)	Bulk Density (g/cm ³)	Fluid Velocity (m/d)	CEC (Unstables) (meq/100g)	CEC (Matrix) (meq/100g)

Zone A2					
1	1.700	2.32	.0017	.037	1.08
2	1.300	2.27	.0022	.037	.855
3	0.500	2.25	.012	.069	.855
4	0.090	1.92	.469	.022	.001
5	0.065	1.83	1.06	.019	.001
6	0.054	1.92	.170	.037	.001
7	0.172	2.00	.060	.050	.001
8	0.070	2.00	.104	.037	.001
9	0.379	2.18	.040	.024	2.16
10	3.170	2.44	5.46E-4	.028	6.60
Zone B4					
1	0.238	2.08	0.078	.094	3.510
2	0.432	2.21	0.012	.065	0.789
3	0.385	2.18	0.023	.065	0.789
4	0.424	2.22	0.012	.119	2.967
5	2.400	2.39	0.004	.025	3.148
6	0.257	2.07	0.078	.065	0.001
7	0.427	2.23	0.012	.252	2.630
8	0.431	2.20	0.012	.001	1.000
9	0.500	2.23	0.023	.001	0.050
10	0.130	2.07	0.078	.001	0.181
11	0.060	1.83	1.246	.001	0.543
12	0.035	1.62	4.738	.001	0.500

4. CONCLUSIONS AND RECOMMENDATIONS

The goals of this study set out in the terms of reference have been met to a considerable degree. The existing equations which relate the textural parameters derived from a size distribution of "clean" sands to their permeability can be applied with suitably modified shape coefficients to the prediction of the permeability of silt- and clay- rich sands. The dispersivity of such sands may also be estimated from their uniformity coefficient and mean grain size by a simple relationship derived from the experimental work of Klotz et al. (1980). Similar modifications and derived relationships have been developed from the theoretical work of Brace (1977), the experiments of Legatski and Katz (1967) and other related studies to predict the permeability and dispersivity of sandstones from their formation factor and detrital and authigenic mineralogy. The mineralogy of a clastic sediment generally can be a fairly accurate predictor of hydraulic and transport properties if it is known in sufficient detail.

Finally, a "method- of- characteristics" (MOC) model for the solution of (1) has been extended to predict the distribution of mass in a fluid subject to cation exchange in a steady, unidirectional flow domain in one and two dimensions. Several examples of the sensitivity of the model output to variations in permeability and CEC consequent upon the grain size distribution and mineral composition of the porous medium have been demonstrated for a variety of

artificial and natural sands and sandstones.

In its present form the MOC model may be used in appropriate circumstances for "generic data base" modelling, (Anderson, 1983), as a preliminary screening technique to estimate the feasibility of proposed hazardous waste disposal sites. The ability of MOC to model cation exchange in steady groundwater flow also suggests the possibility of similar application to screening the feasibility of aquifer restoration schemes following the solution mining of uranium in sandstone bodies, (Warner, 1981). Certain miscible displacement processes used in secondary and tertiary oil recovery could be simulated with the MOC technique, (Smith, 1978; Somerton and Radke, 1983).

The success of (2), (12)/(14), and (31)/(35) in predicting, respectively, the porosity, permeability and dispersivity of clastic sands and sandstones is shown by the ability to match these quantities measured on a wide variety of samples. However, their predictive capability could be enhanced, or better relationships could be derived, by specific experimentation to obtain the geometric, lithological or mineralogical information needed to demonstrate the postulated relationships in a completely unequivocal manner. For instance, the use of modern techniques of shape analysis using automated image analysis methods and algorithms would allow one to compute the packing density of assemblages of non-spherical sand and silt particles, (Melloy, 1984). Similarly, new developments



in electron microscopy coupled with existing stereologic techniques make feasible the detailed determination of grain and pore geometry and the shapes of authigenic minerals within the pore space, (Haas et al. 1967a, 1967b; Serra 1967, 1972; Daniel and Nicholson, 1977; Murphy et al., 1977; Bisdom and Thiel, 1981; Jongerius and Bisdom, 1981; Lin 1982a,b). In turn, application of these techniques would permit more elaborate evaluation of shape coefficients for permeability determination.

Nevertheless, the main gap in experimental data exists for measurements of longitudinal and transverse dispersivity in clay-rich sandstones. For example, there is no way of verifying the postulated effects of micro- and macroporosity on the dispersion attributes of the Belly River Sandstone samples without actual measurements. The experiments of Deans (1963) and Coates and Smith (1964) indicated that these effects could be observed even on "clean" sandstones. It would be useful to repeat these experiments on clay-rich sandstones, coupling them with detailed stereological and mineralogical examinations of the core samples. Analytical solutions are available to model the applicable transport equation with the necessary source and reaction terms, (Van Genuchten and Alves, 1982).

The version of the MOC model currently implemented on the University of Alberta Amdahl 5860 computer works well in the simple cases to which it has been applied in this study. However, improvements to the code would be advisable if the

program is to be made completely transportable. For instance, the interval halving technique used in the ion exchange subroutine for the computation of the equilibrium concentration of ions in the solution and on the exchangers occasionally fails to converge after reaching the programmed limit of 100 iterations. This condition occurs most commonly in the situation of three exchangers with greatly differing cation exchange capacities. At the cost of increased programming complexity, the use of more efficient numerical procedures for solving the system of equations (54) through (56) should be investigated.

Another area requiring further attention is the determination of the optimum combination of space and time increments to maintain stability of the numerical solution to the dispersion equation. Currently these parameters (Δt , Δx and Δz) are read in as data and are fixed for each run. They are altered by trial and error until a stable solution is obtained. Instability in the solution is shown by oscillation in the relative concentration values which die away in the direction of transport. These oscillations are a consequence of too large a time step for the velocity and space increments, so that an "overshoot" of mass occurs into cells further along the direction of transport. The condition is usually cured by reducing the size of the time step. However, too small a time step is computationally inefficient and can also yield inaccurate results. The time and space increments are sensitive to the flow velocity:

consequently, layered domains with large inter-layer velocity contrasts are most susceptible to this condition.

Although the MOC program is not coupled with a groundwater flow model in this study, the appropriate coding for two dimensional flow can be implemented without excessive effort. Successful implementation of this change, however, would require that the time and space increment problem be solved, because the hydraulic heads and hence the fluid velocities would change at each time increment of the flow model.

Finally, the two-dimensional MOC model could be used to explore the simulation of mass transport in vertically and laterally heterogeneous clastic sediments. The application in the present work to the simulation of mass transport in various sedimentary and diagenetic facies of the Muddy Formation suggests the potential for obtaining the transport properties of clastic sedimentary sequences from their sedimentology, lithologies and diagenetic history. Such an approach is commonly used by petroleum geologists to evaluate petroleum reservoirs in terms of their porosity, permeability and likely response to secondary recovery operations, (Harris and Hewitt, 1977; Morgan et al., 1977; Wadman et al., 1979). Thus, the methodology is readily available and could be adapted to the needs of hydrogeology without undue effort.

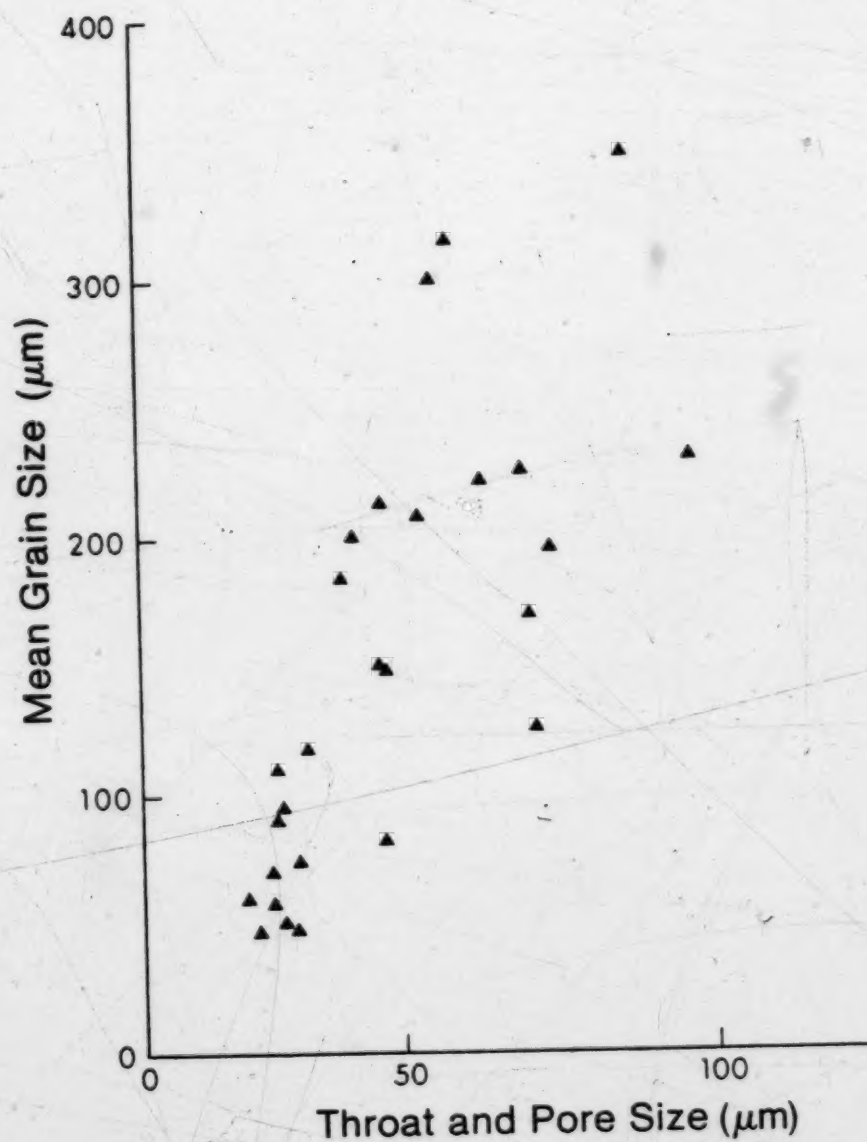


Figure 1. Mean Grain Size versus Throat and Pore Size for Clastic Sandstones

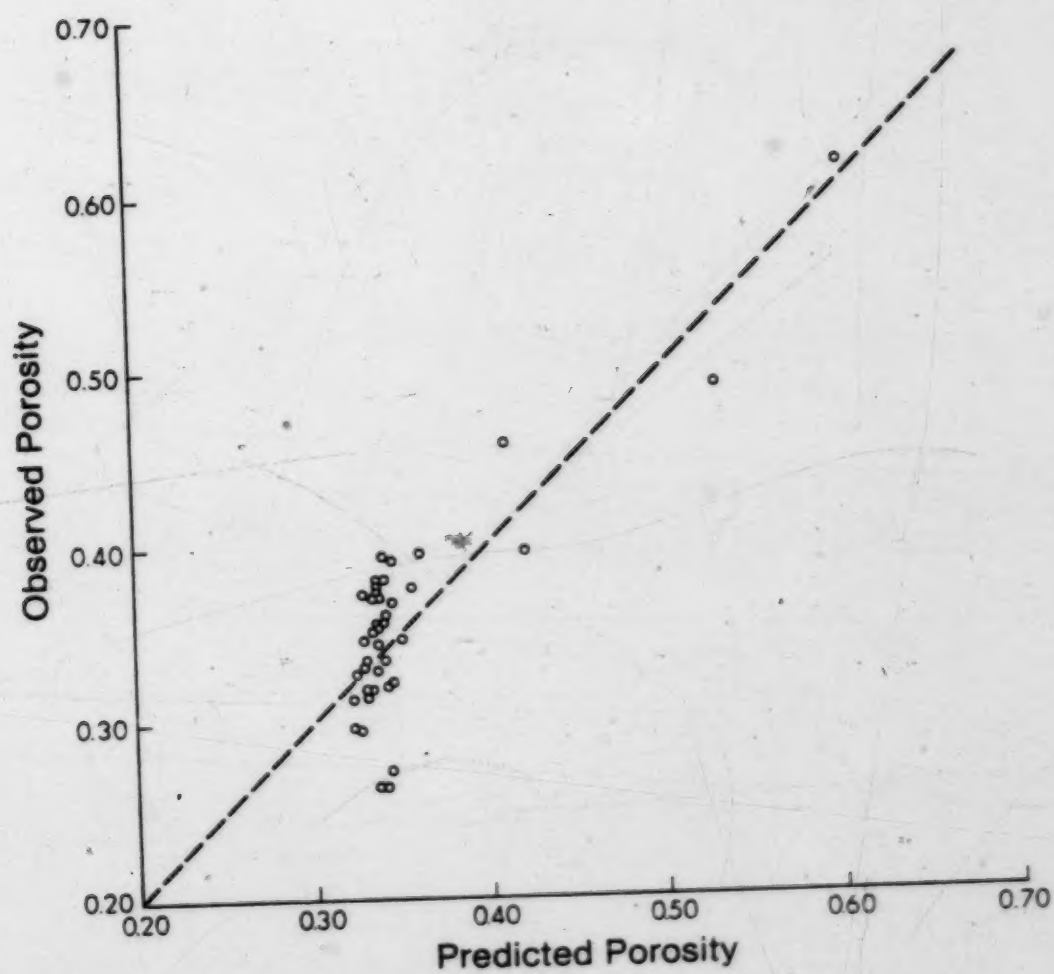


Figure 2. Prediction of Porosity with (2)

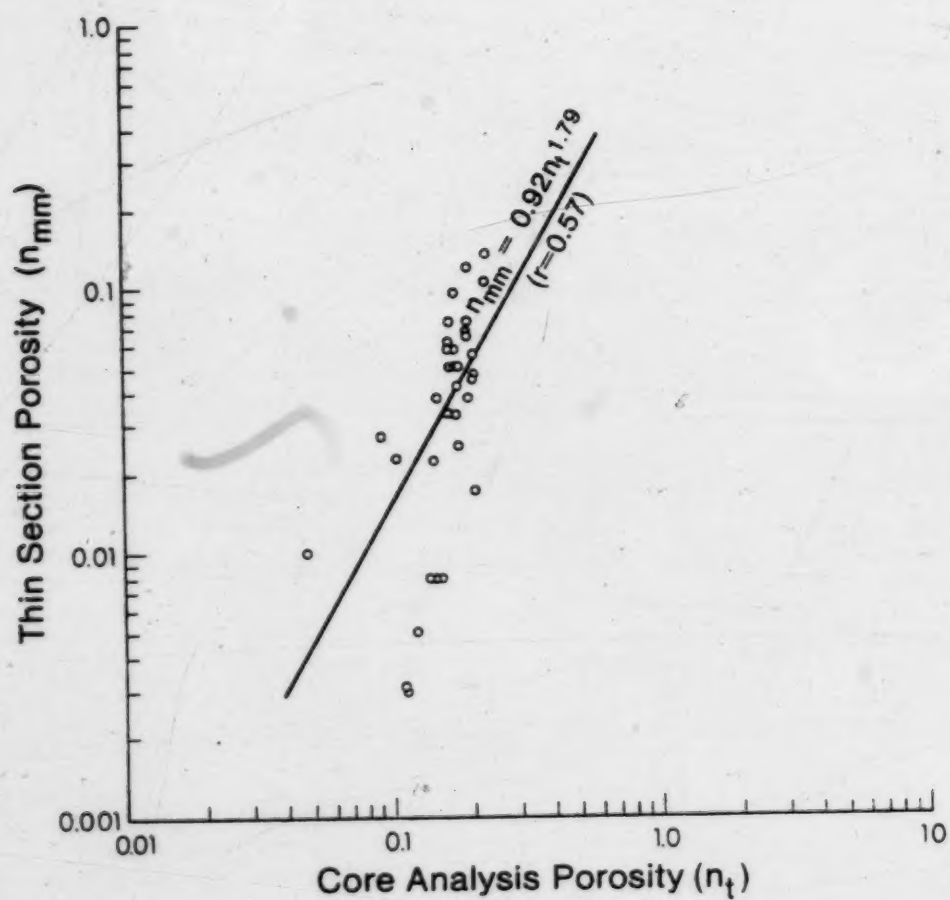


Figure 3. Comparison of Porosity from Thin Sections and Core Analysis, Basal Belly River Sandstone

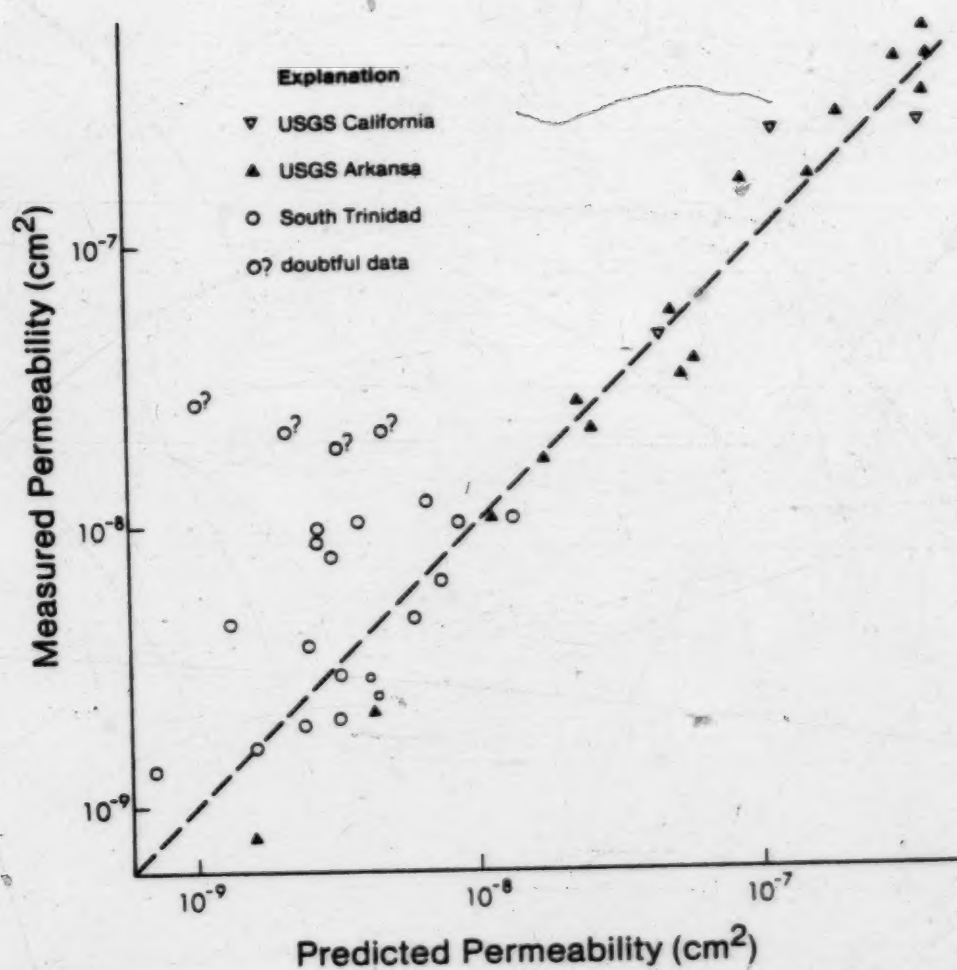


Figure 4. Prediction of Permeability of Silty Sands

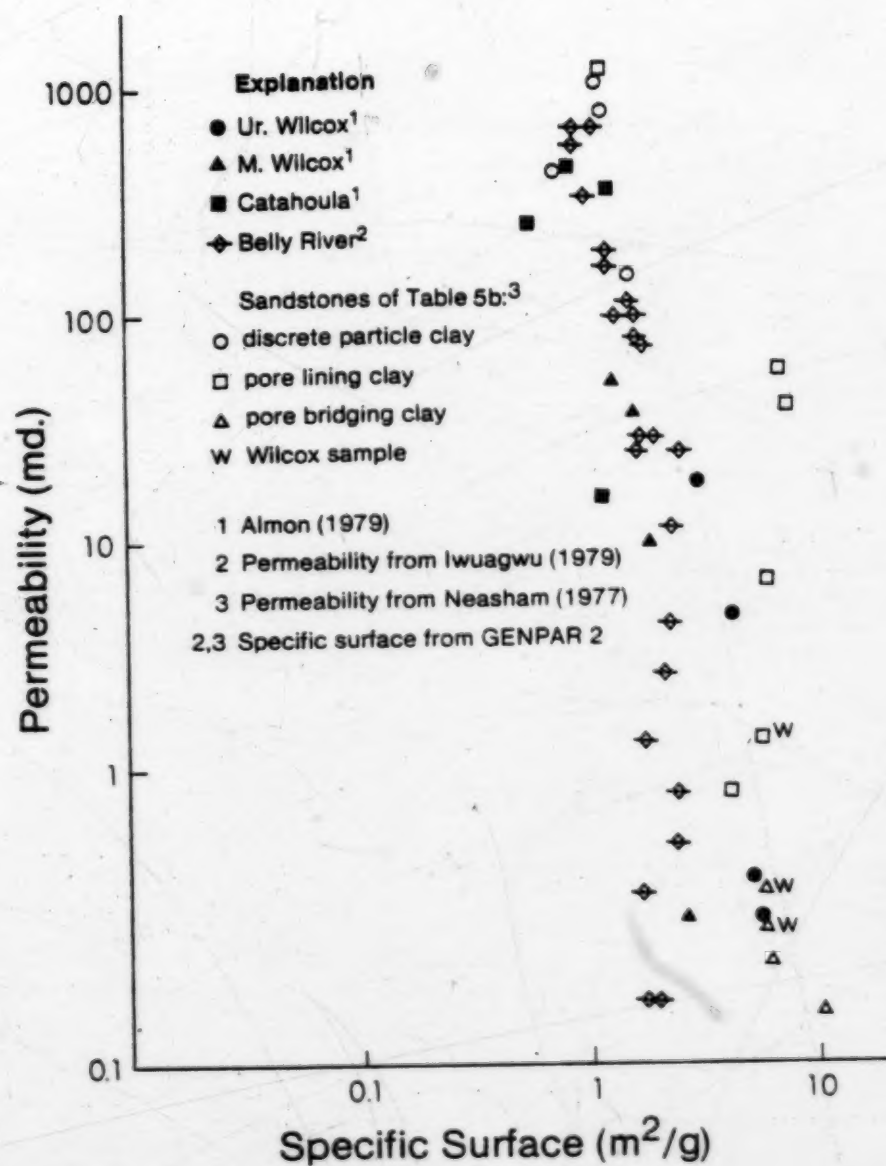


Figure 5. Relationship between Specific Surface and Permeability of Sandstones

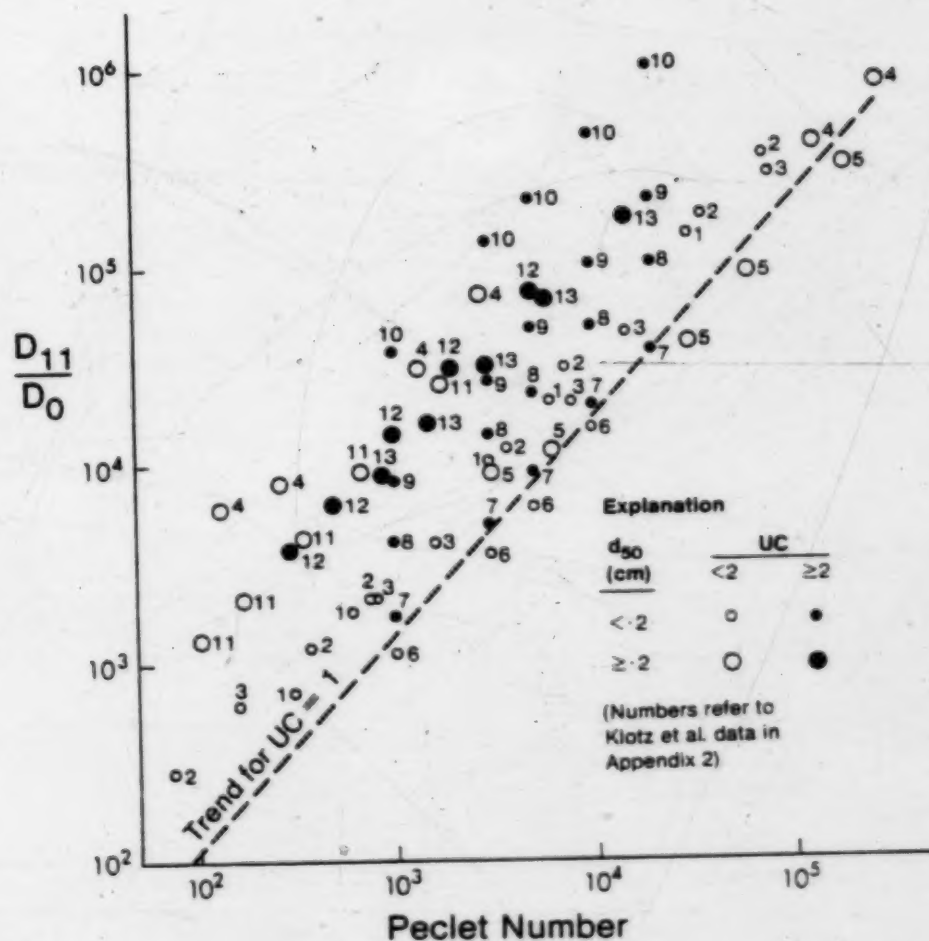


Figure 6. Relationship between Peclet Number and Dispersion for Sands and Gravels

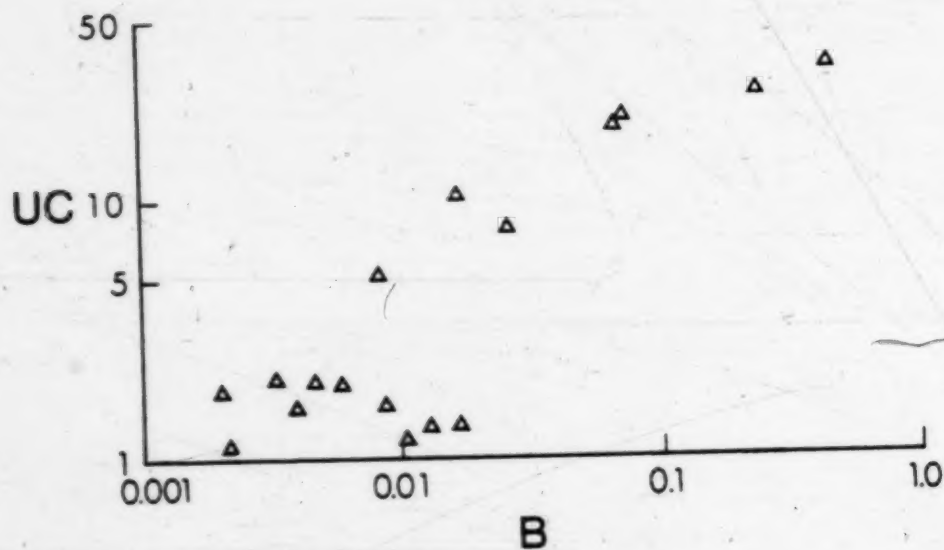
A. B versus d_{50} B. B versus UC

Figure 7. Relationships between B and Parameters of a Grain Size Distribution:

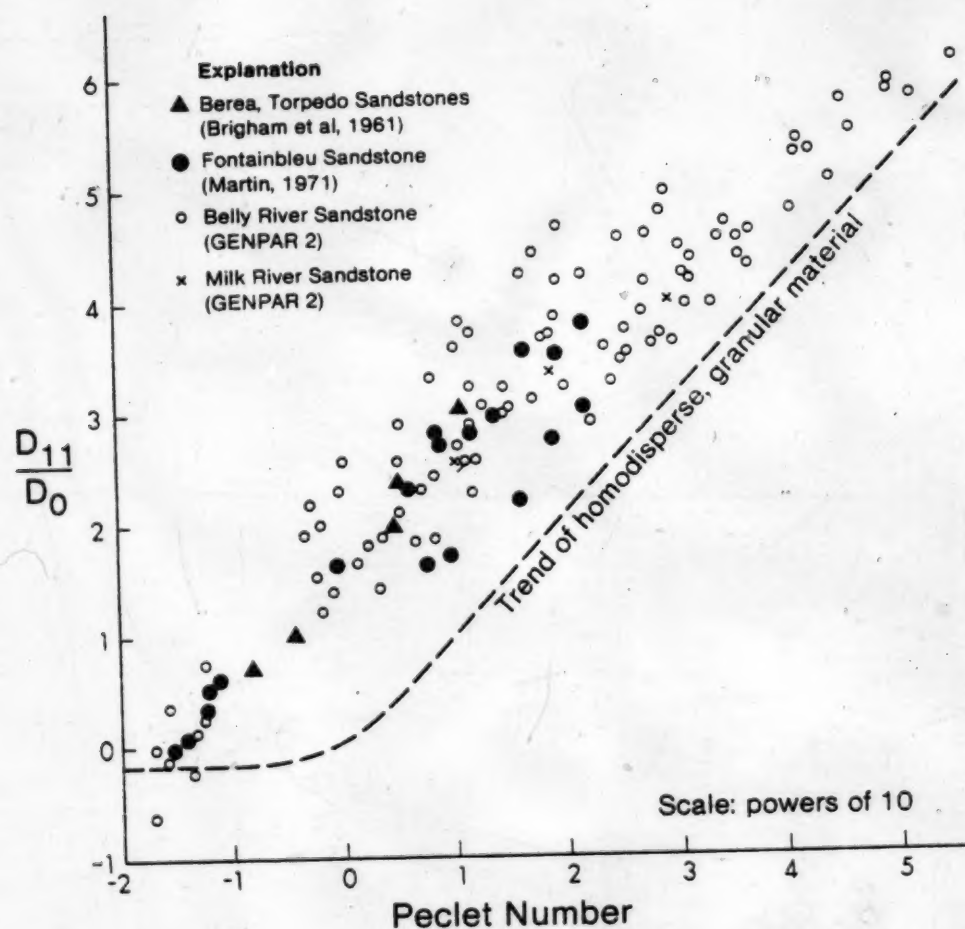


Figure 8. Relationship between Peclet Number and Dispersion for Various Sandstones

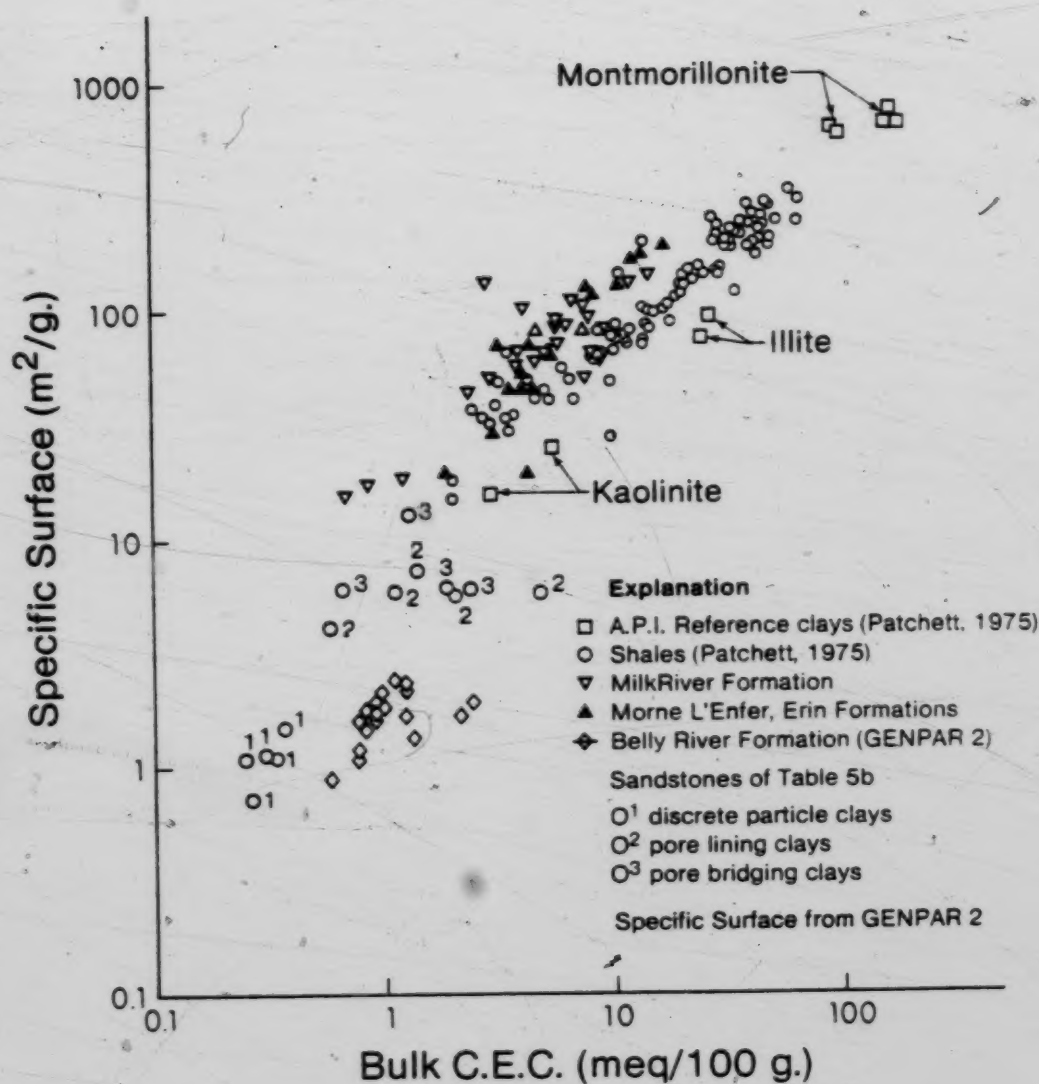


Figure 9. Specific Surface versus Bulk CEC of Various Materials

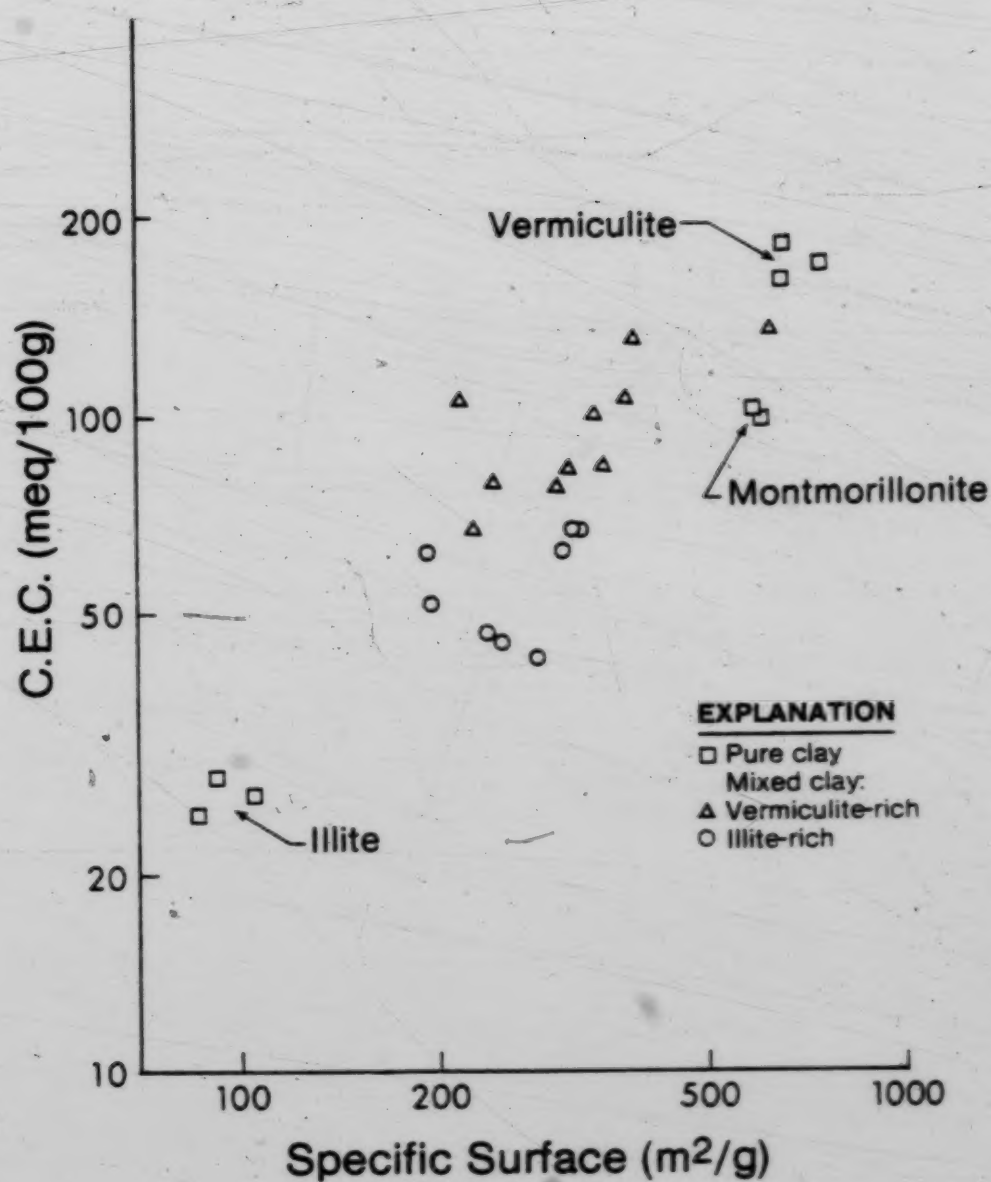


Figure 10. Relationship between Specific Surface and CEC of Expanding Clays

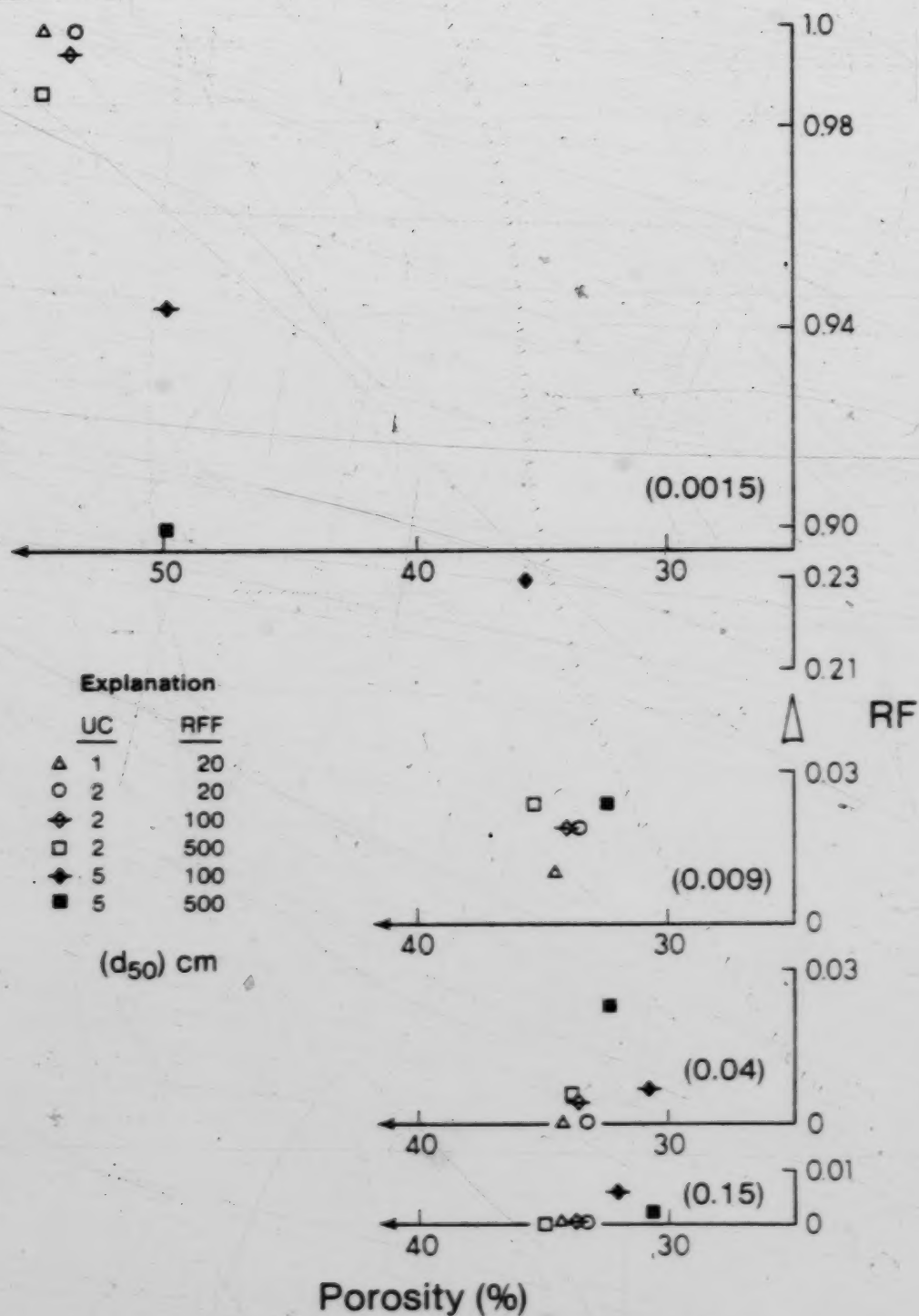


Figure 11. Porosity versus RF of Artificial Sands

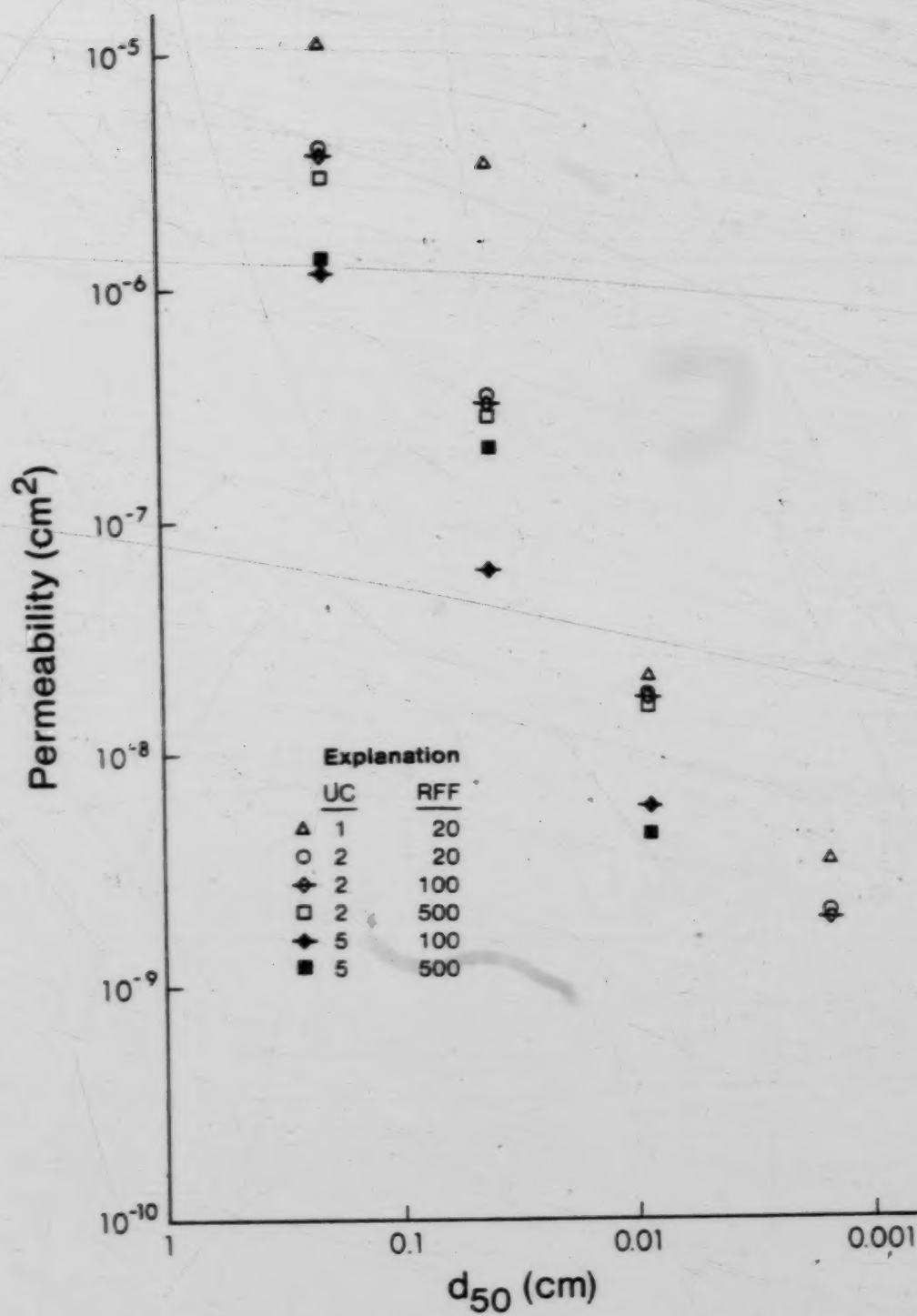


Figure 12. Permeability versus d_{50} of Artificial Sands

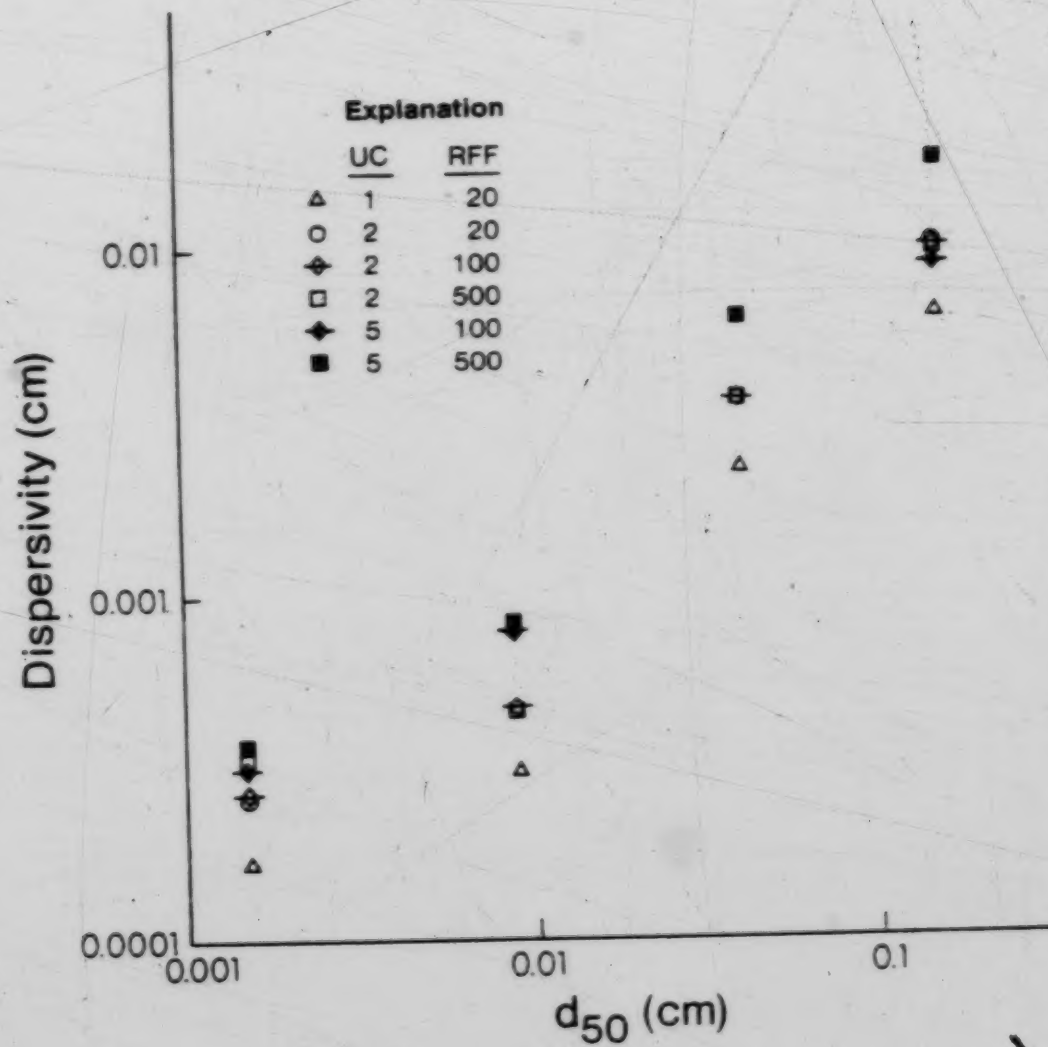


Figure 13. Dispersivity versus d_{50} of Artificial Sands

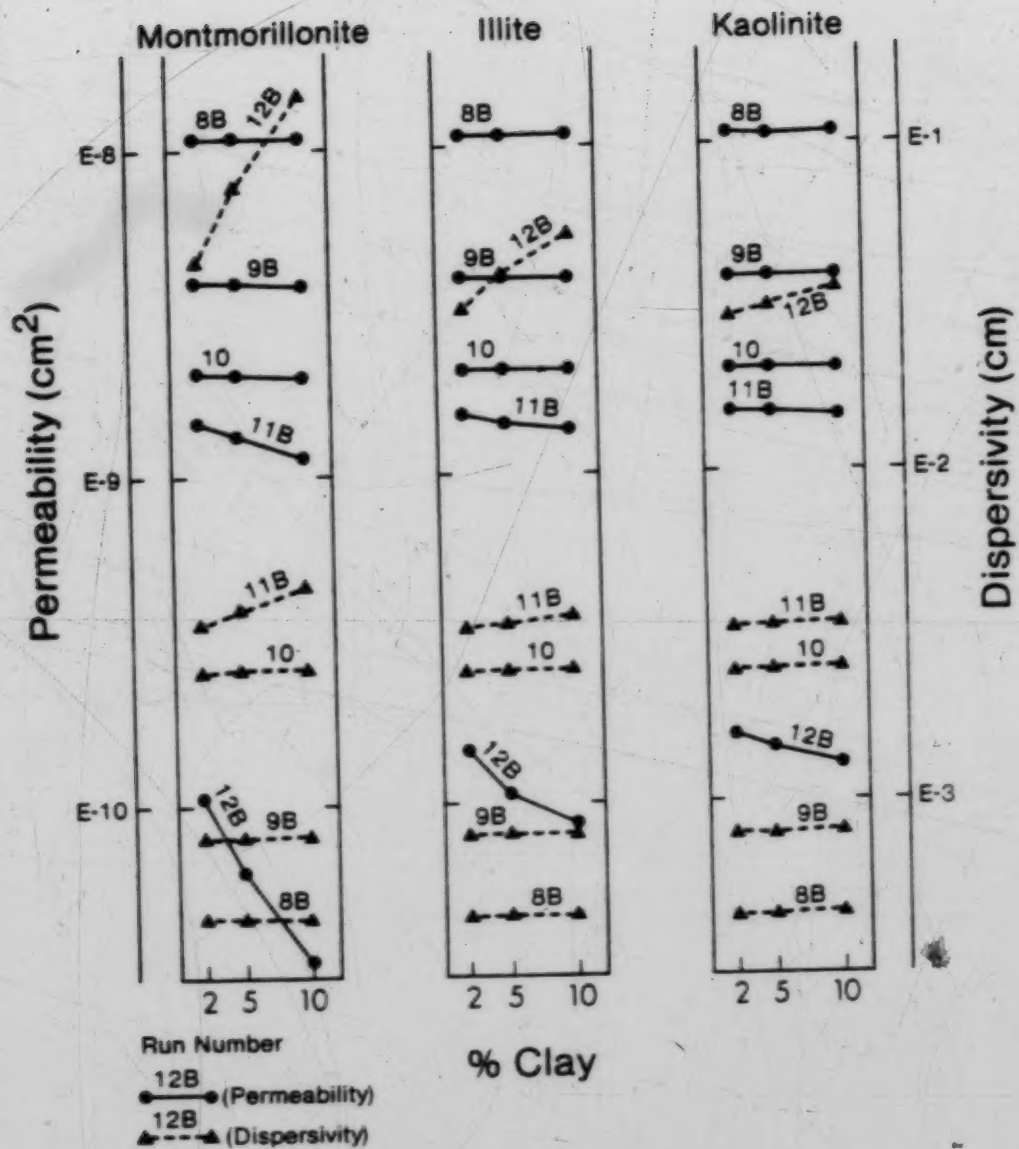


Figure 14. Influence of Clays upon Permeability and Dispersivity of Artificial Sands

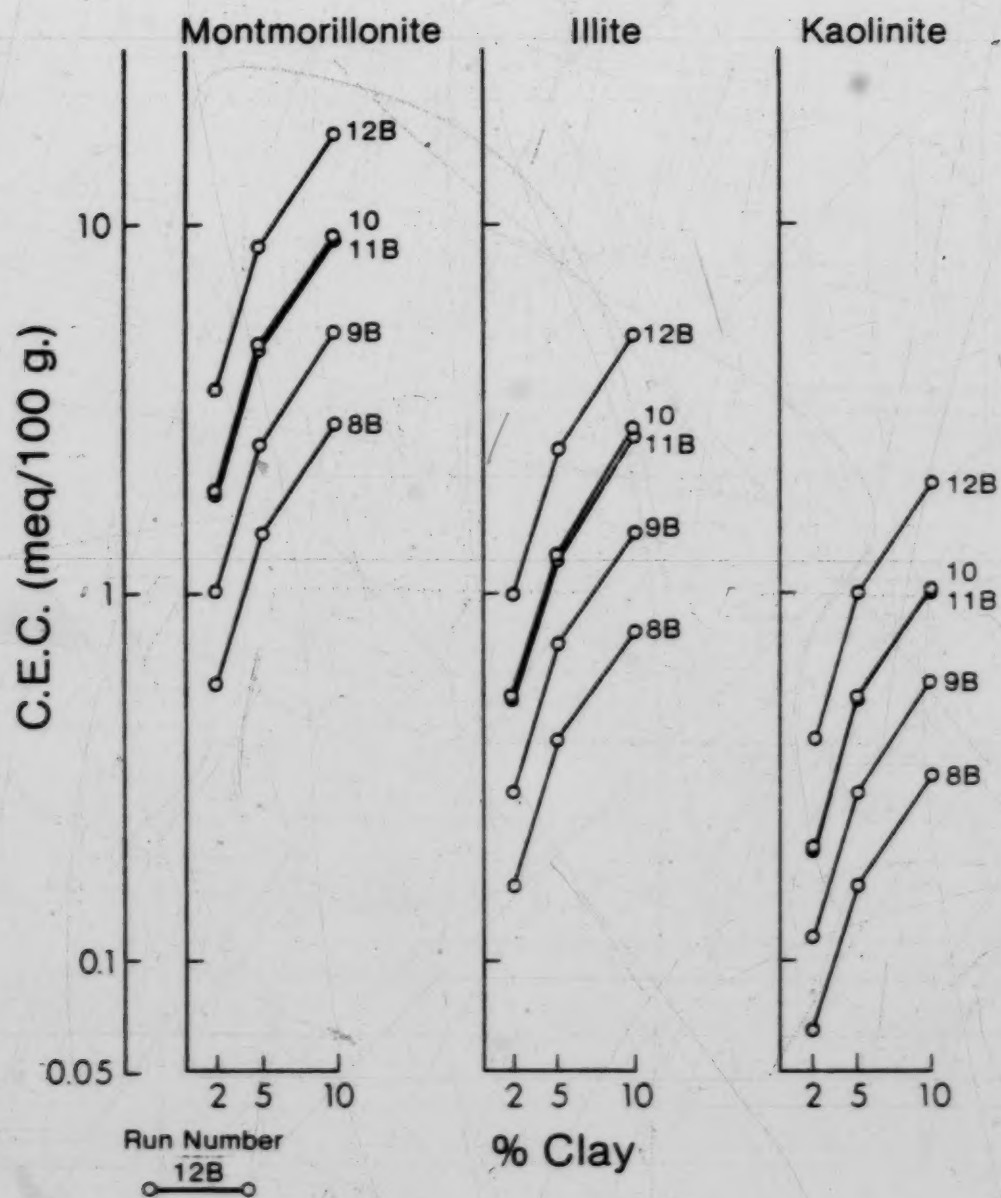


Figure 15. Influence of Clays upon CEC of Artificial Sands

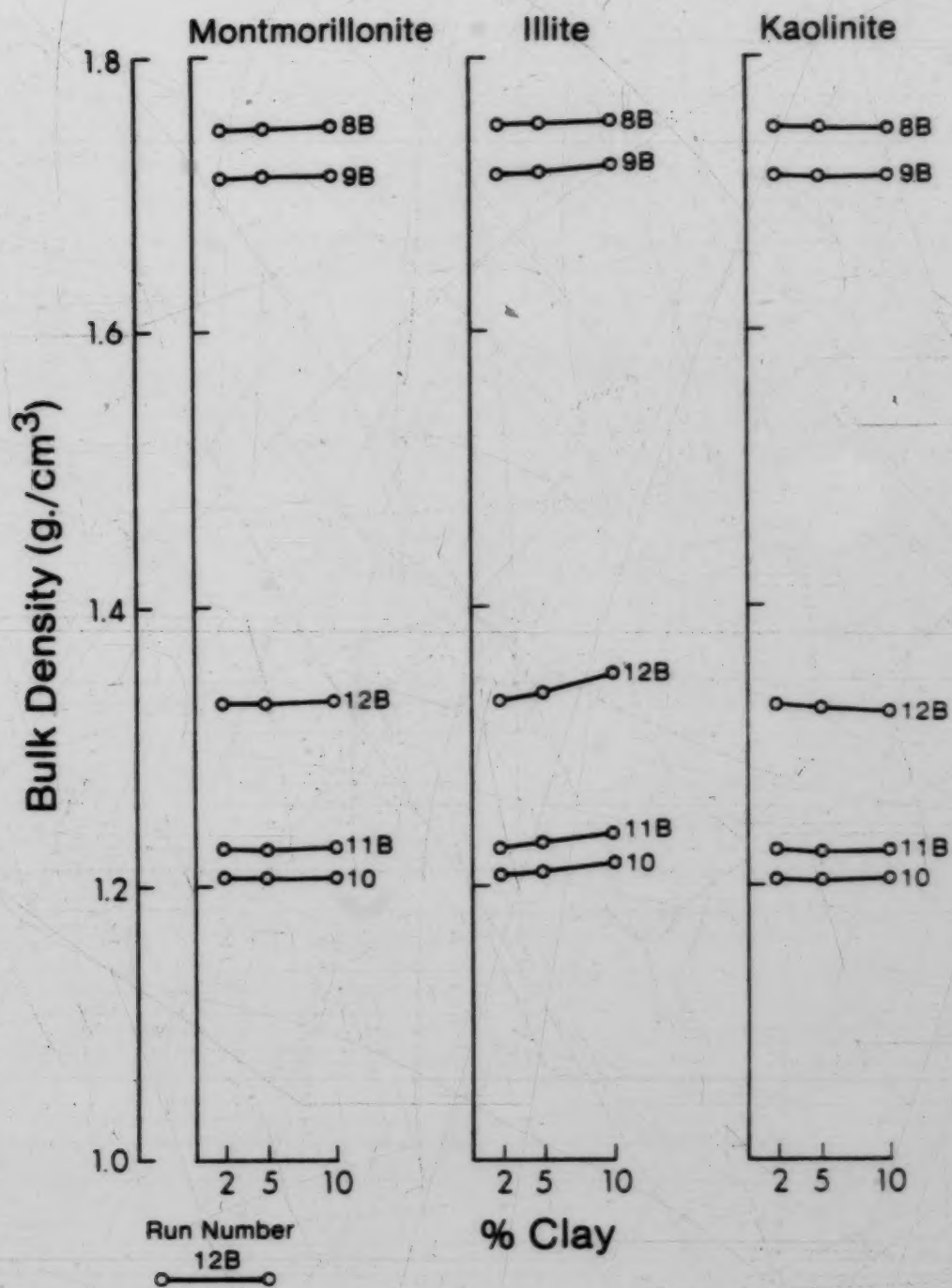


Figure 16. Influence of Clays upon Bulk Density of Artificial Sands

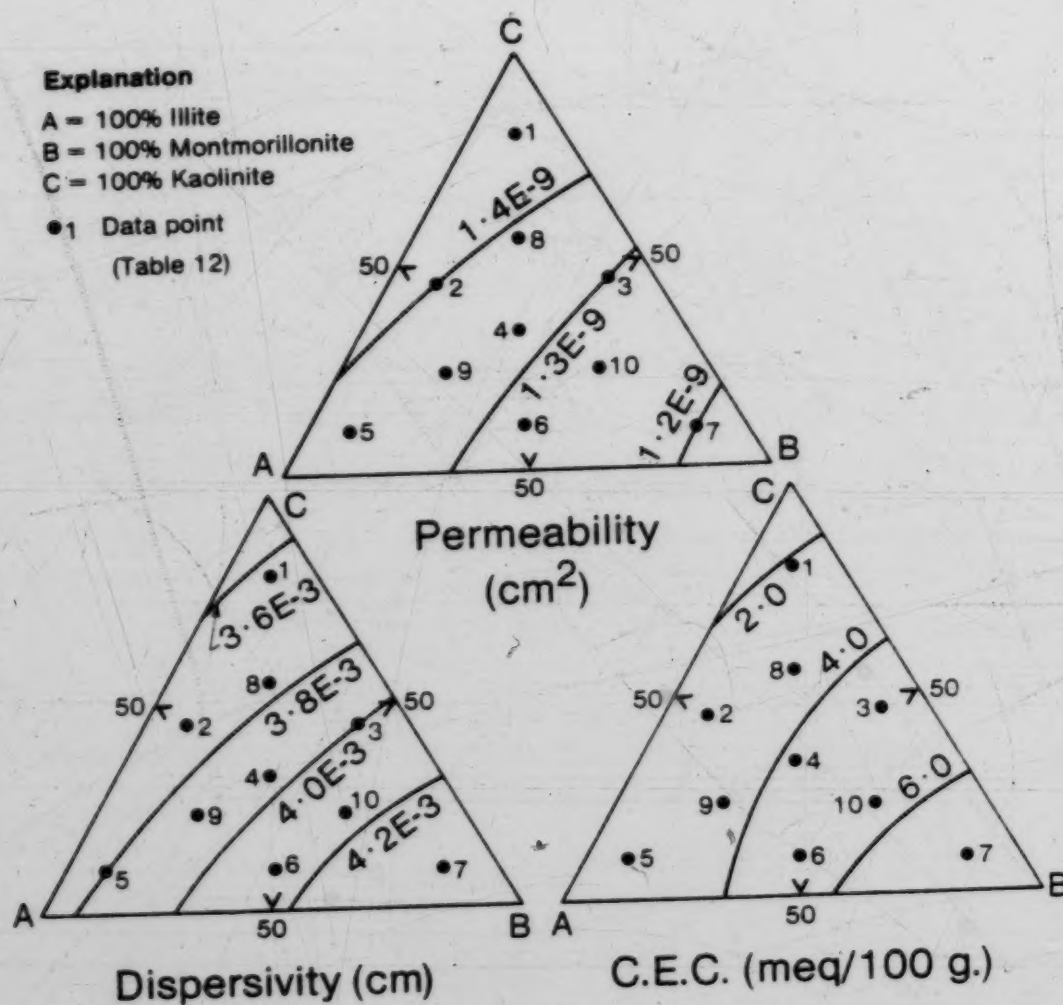


Figure 17. Effect of Mixtures of Clays on Permeability, Dispersivity and CEC of Run 11B

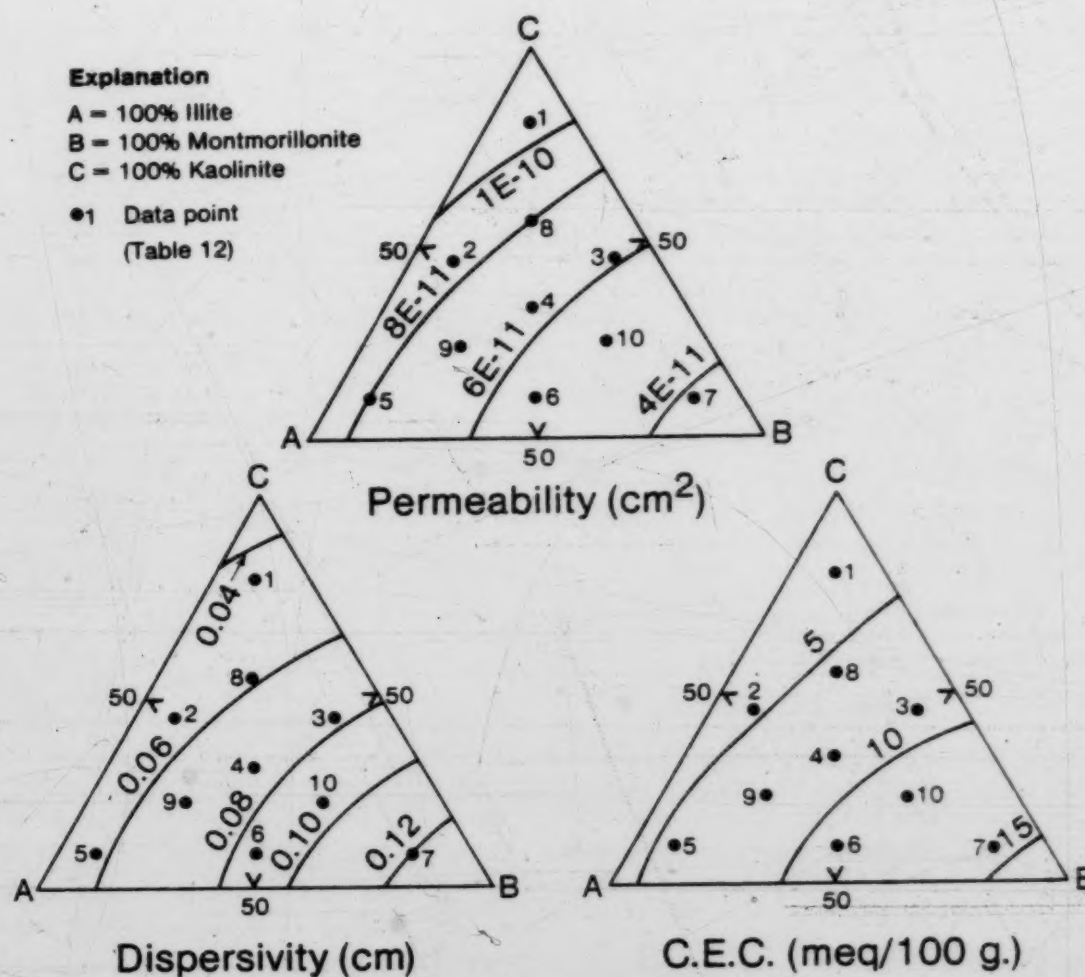


Figure 18. Effect of Mixtures of Clay on Permeability, Dispersivity and CEC of Run 12B

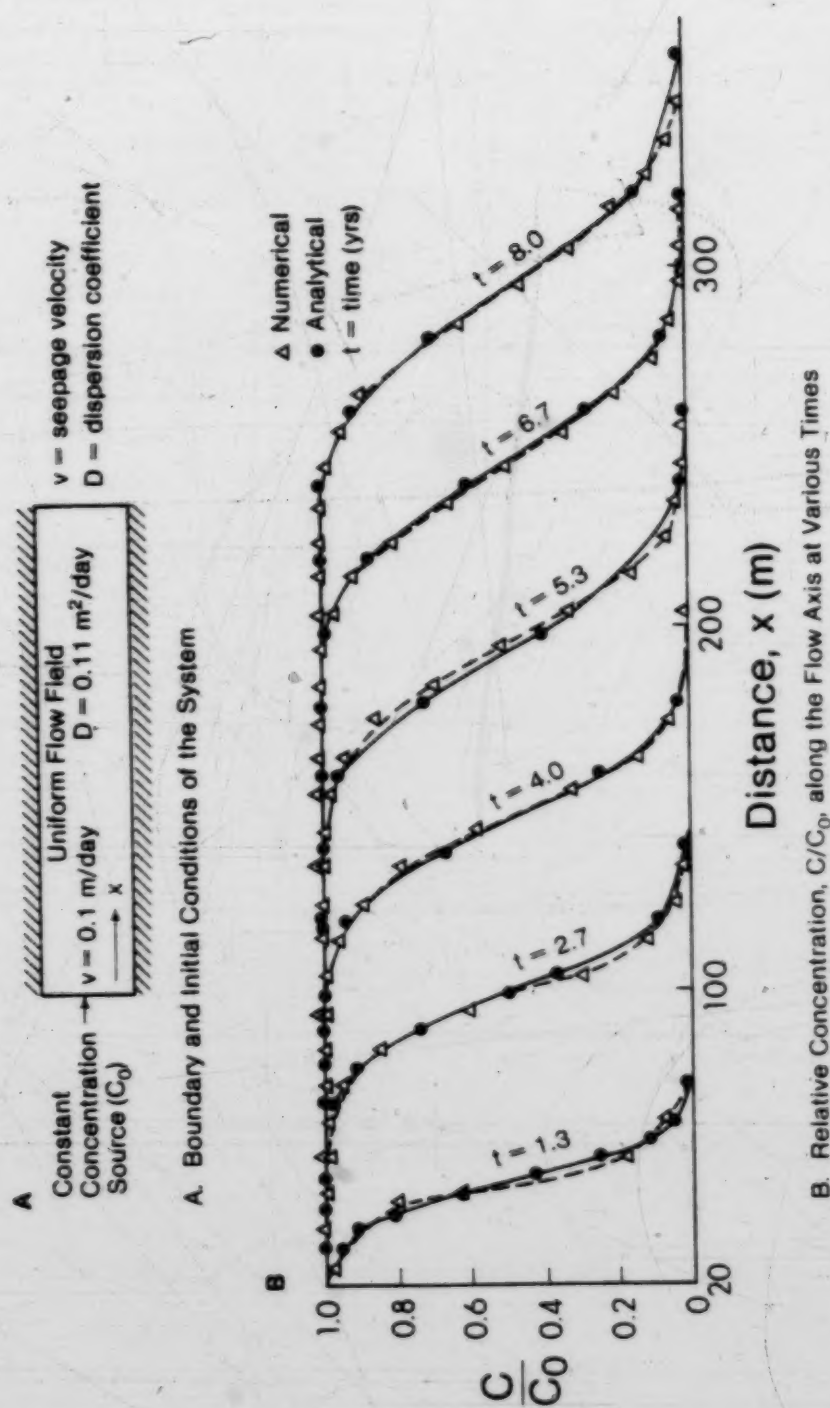


Figure 19. Comparison of the Analytical and Numerical Solutions for One-dimensional Mass Transport without Adsorption

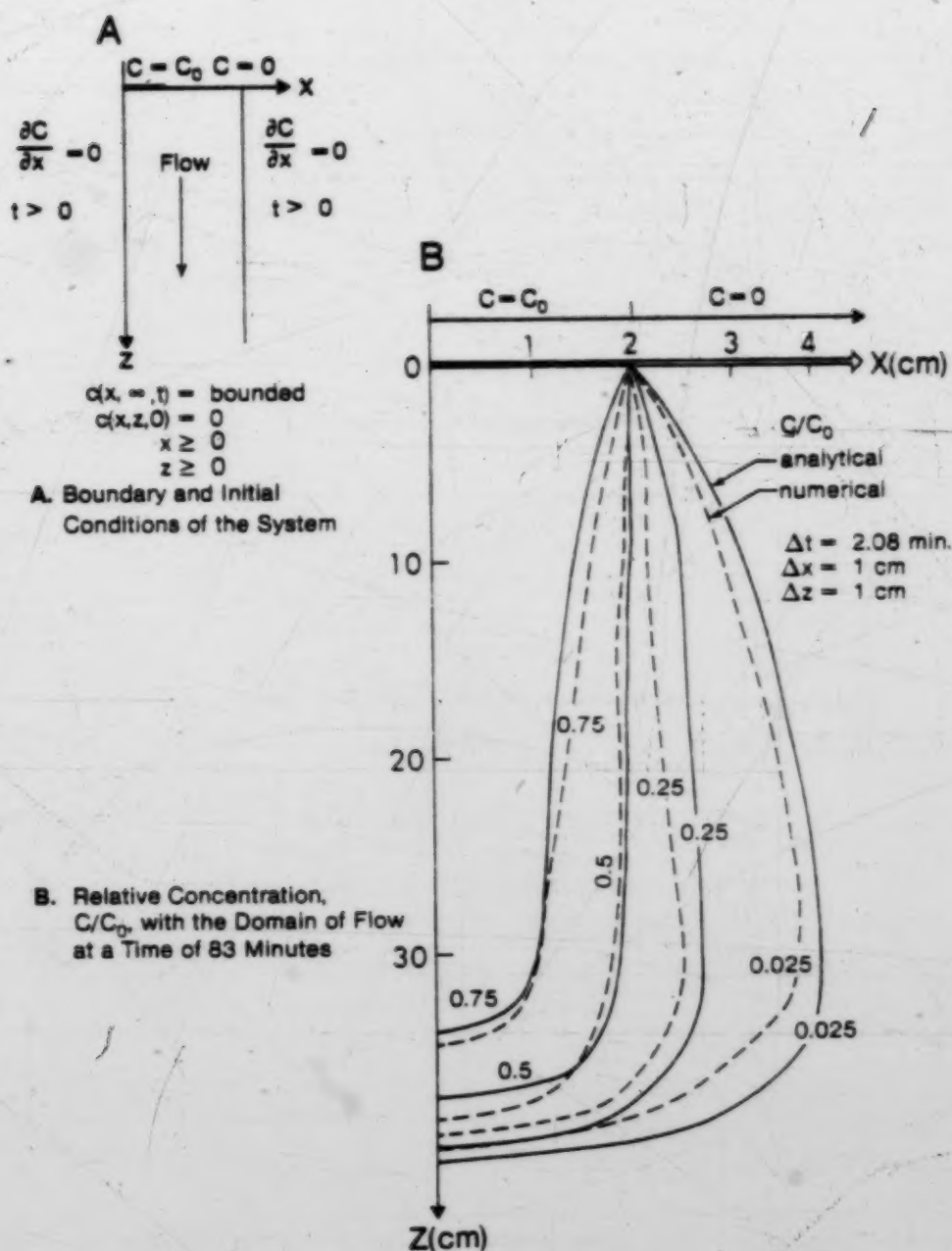


Figure 20. Comparison of the Analytical and Numerical Solutions for Two-dimensional Mass Transport in a Homogeneous Medium without Adsorption

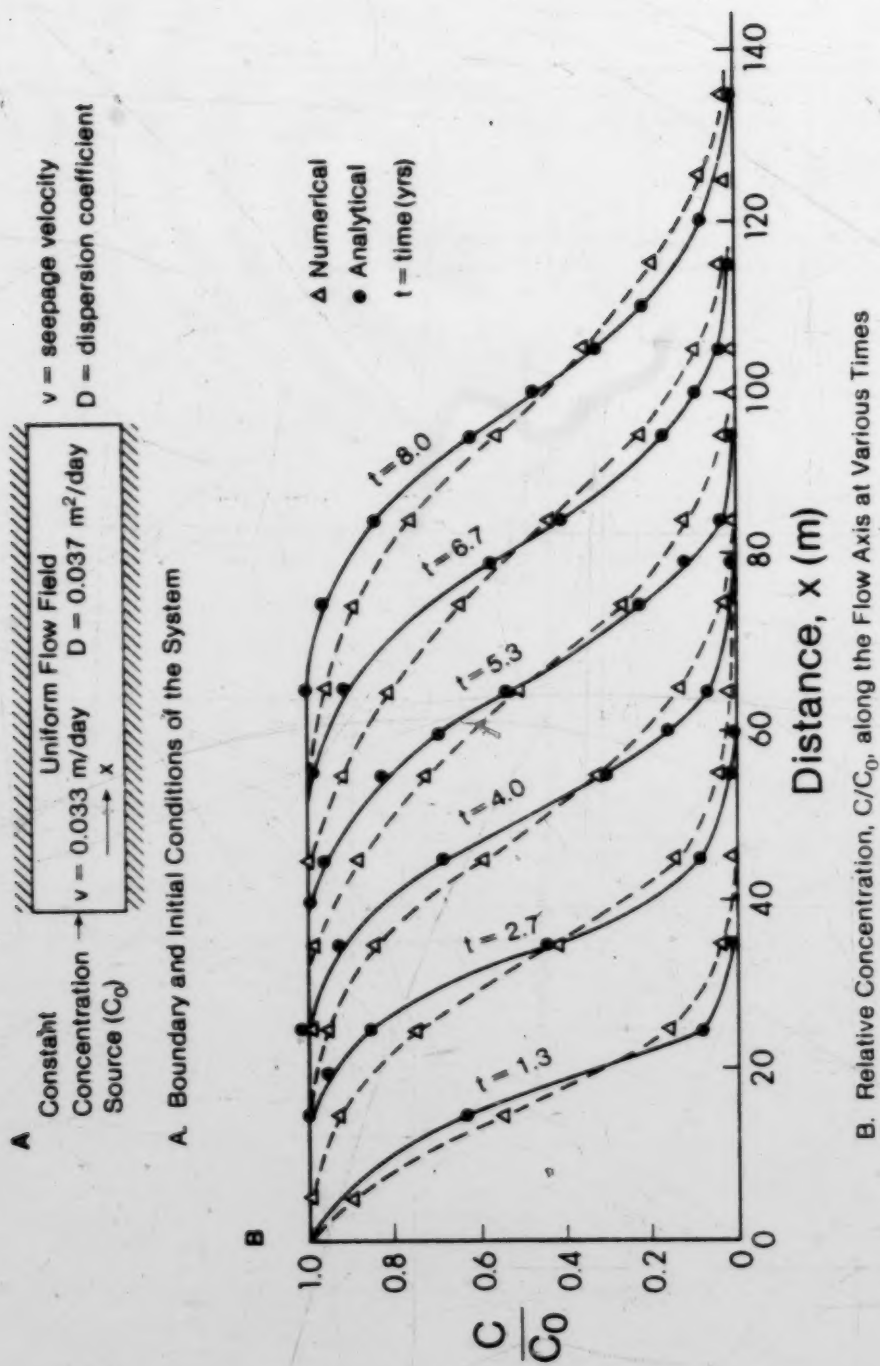


Figure 21. Comparison of the Analytical and Numerical Solutions for One-dimensional Mass Transport with Adsorption:

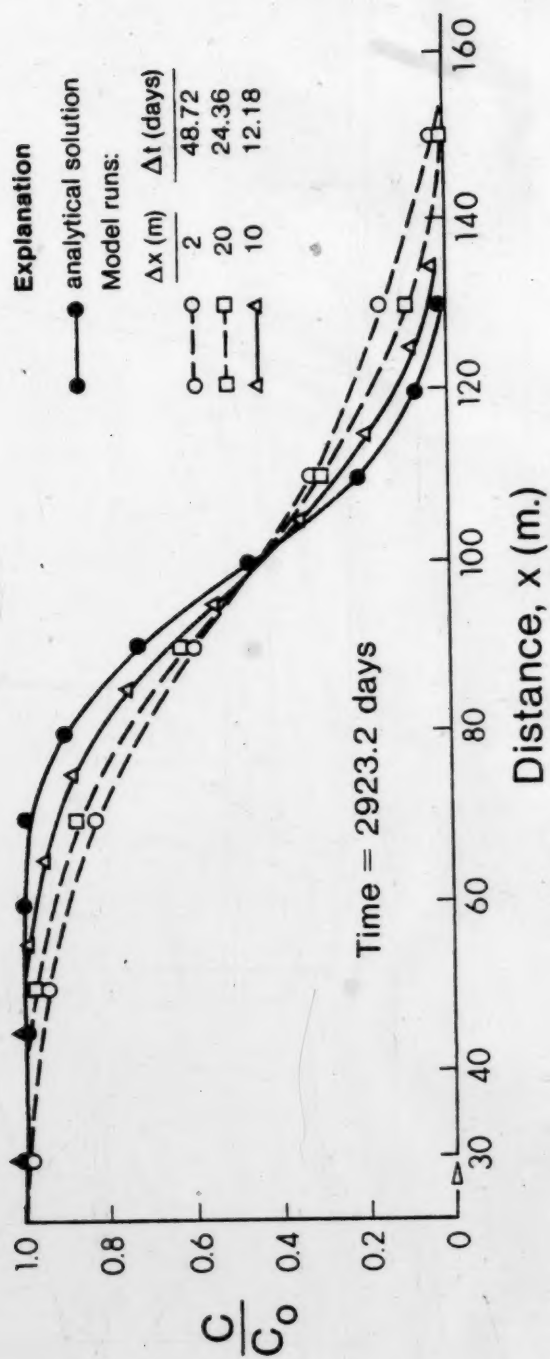


Figure 22. Sensitivity of the MOC Solution for One-dimensional Mass Transport with Ion Exchange to Variation in the Model Parameters

A. Parameters of Each Run

Run	Clay Mineral	K_d	R	Cs^+	Na^+
1	Na-Montmorillonite	3E4	1.01E5	1E-7	2
2	"	9E3	3.04E4	1E-4	2
12	"	5E2	1.69E3	4.0	100
12	"	10	34.75	100	200
21	Na-Kaolinite	350	1.27E3	1E-7	2
22	"	400	1.45E3	3E-4	2
26	"	10	37.25	1E-2	200
27	Na-Illite	8E4	2.63E4	1E-7	2
30	"	8.2E2	2.50E3	2E-4	200

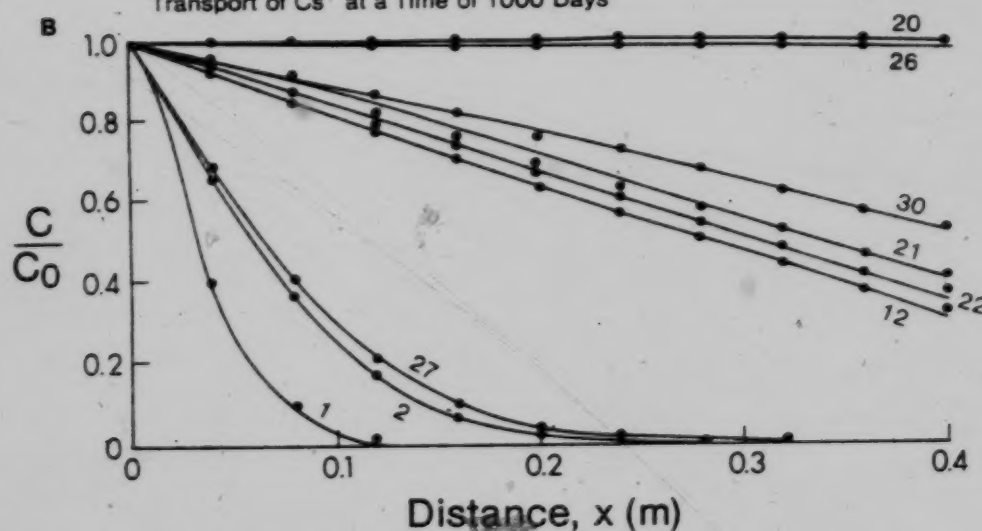
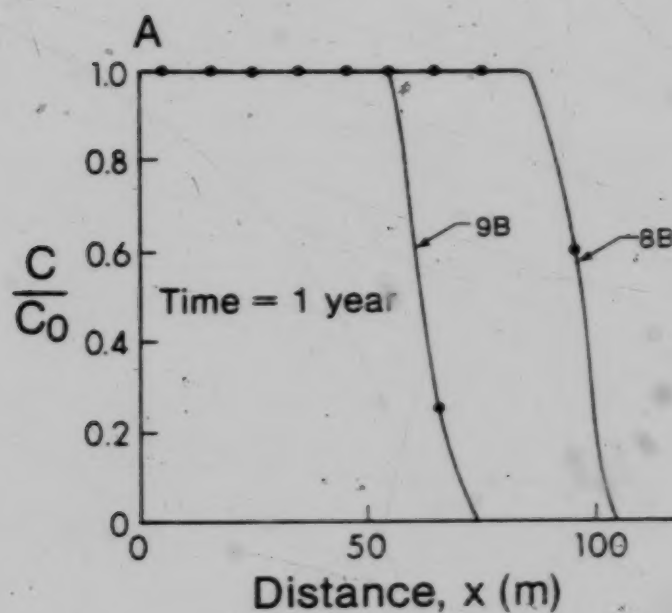
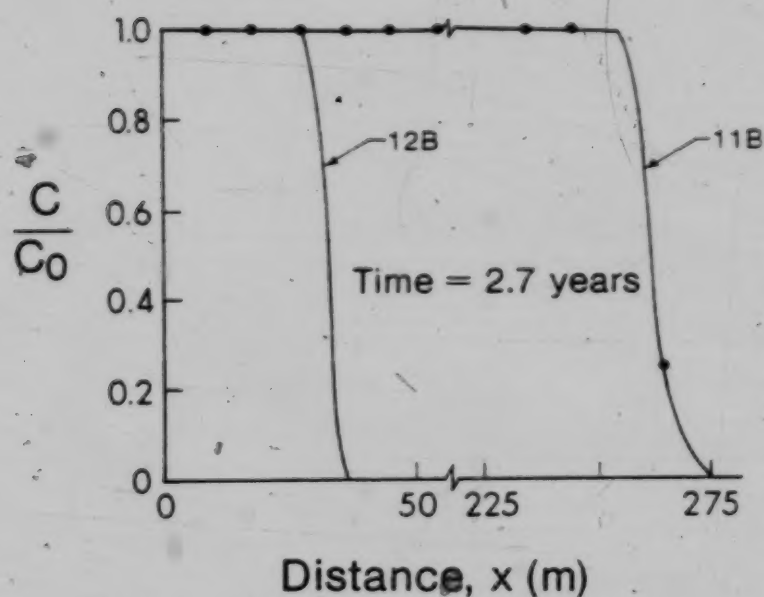
B. Relative Concentration, C/C_0 , along the Flow Axis in One-dimensional Mass Transport of Cs^+ at a Time of 1000 Days

Figure 23. Effect of Variations in R, K_d and Concentration of Competing Cation, Na^+ , on Adsorption of Cs^+ on Various Clays:



A. Relative Concentration, C/C_0 , along the Flow Axis in Runs 8B and 9B



B. Relative Concentration, C/C_0 , along the Flow Axis in Runs 11B and 12B

Figure 24. Influence of Mean Grain Size upon One Dimensional Mass Transport in Artificial Sands:

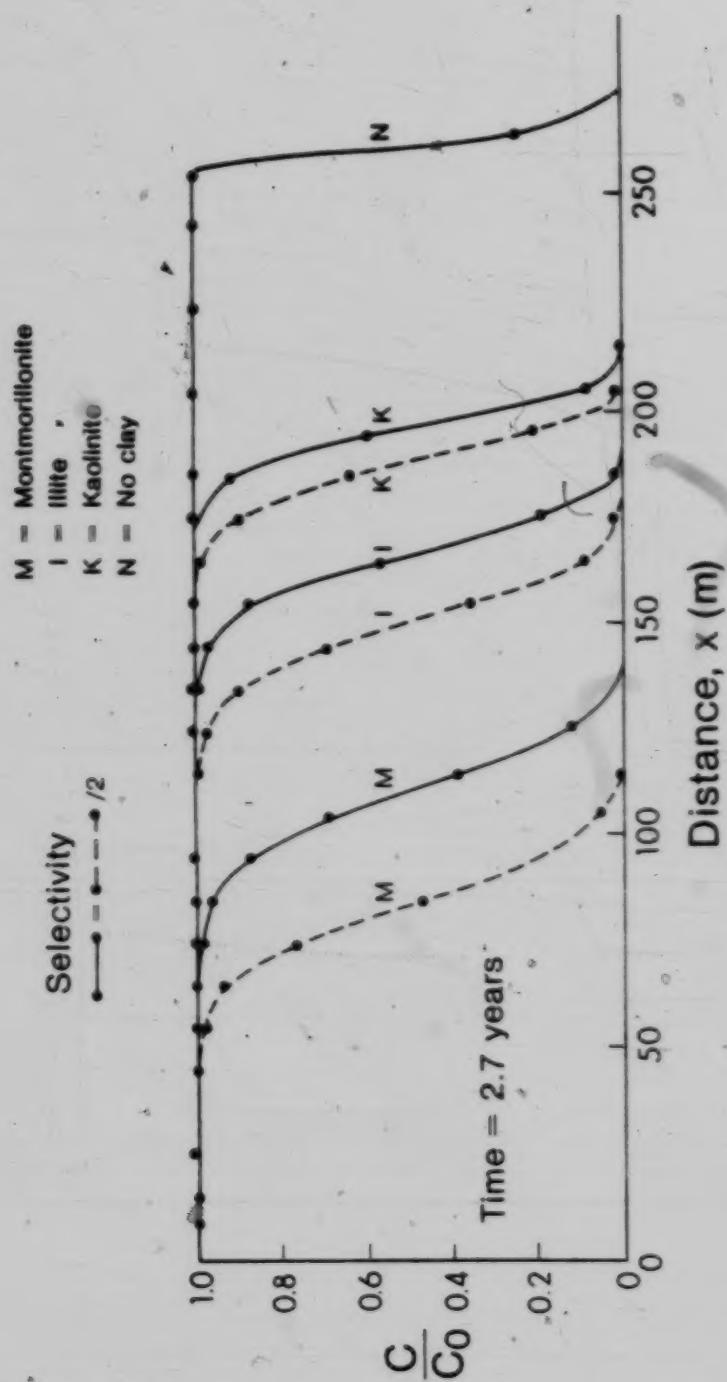


Figure 25. Influence of Single Clays upon the Relative Concentration C/C_0 , along the Flow Axis in Run 11B

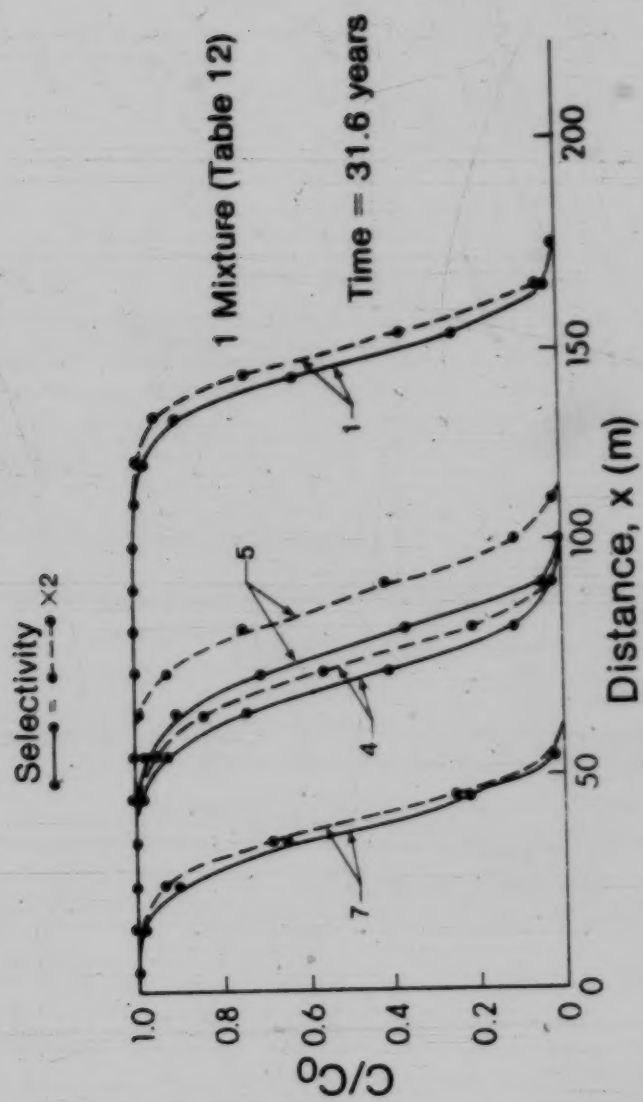
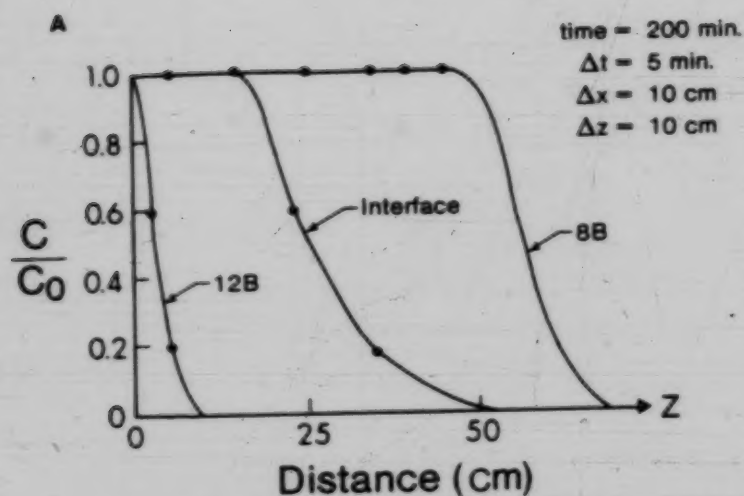
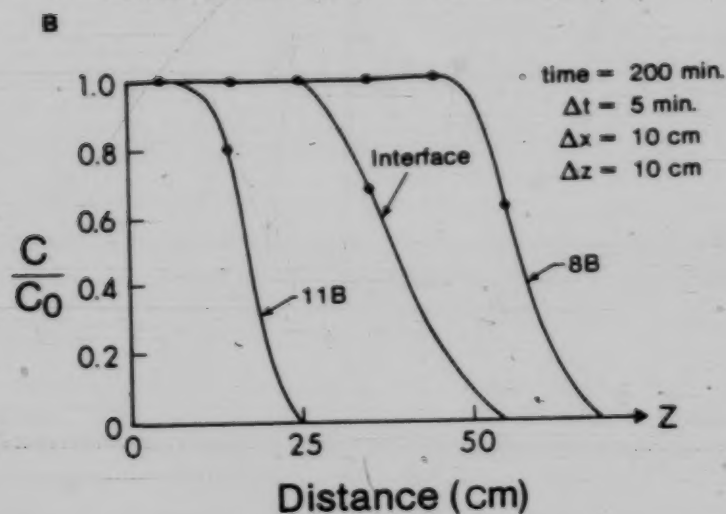


Figure 28. Influence of Mixed Clays upon the Relative Concentration, C/C_0 , along the Flow Axis in Run 12B



A. Relative Concentration, C/C_0 , within Each Layer and at the Interface between Layers for Runs 8B/12B



B. Relative Concentration, C/C_0 , within Each Layer and at the Interface between Layers for Runs 8B/11B

Figure 29. Effect of Contrast in Layer Properties upon Two-dimensional Mass Transport in Layered Media:

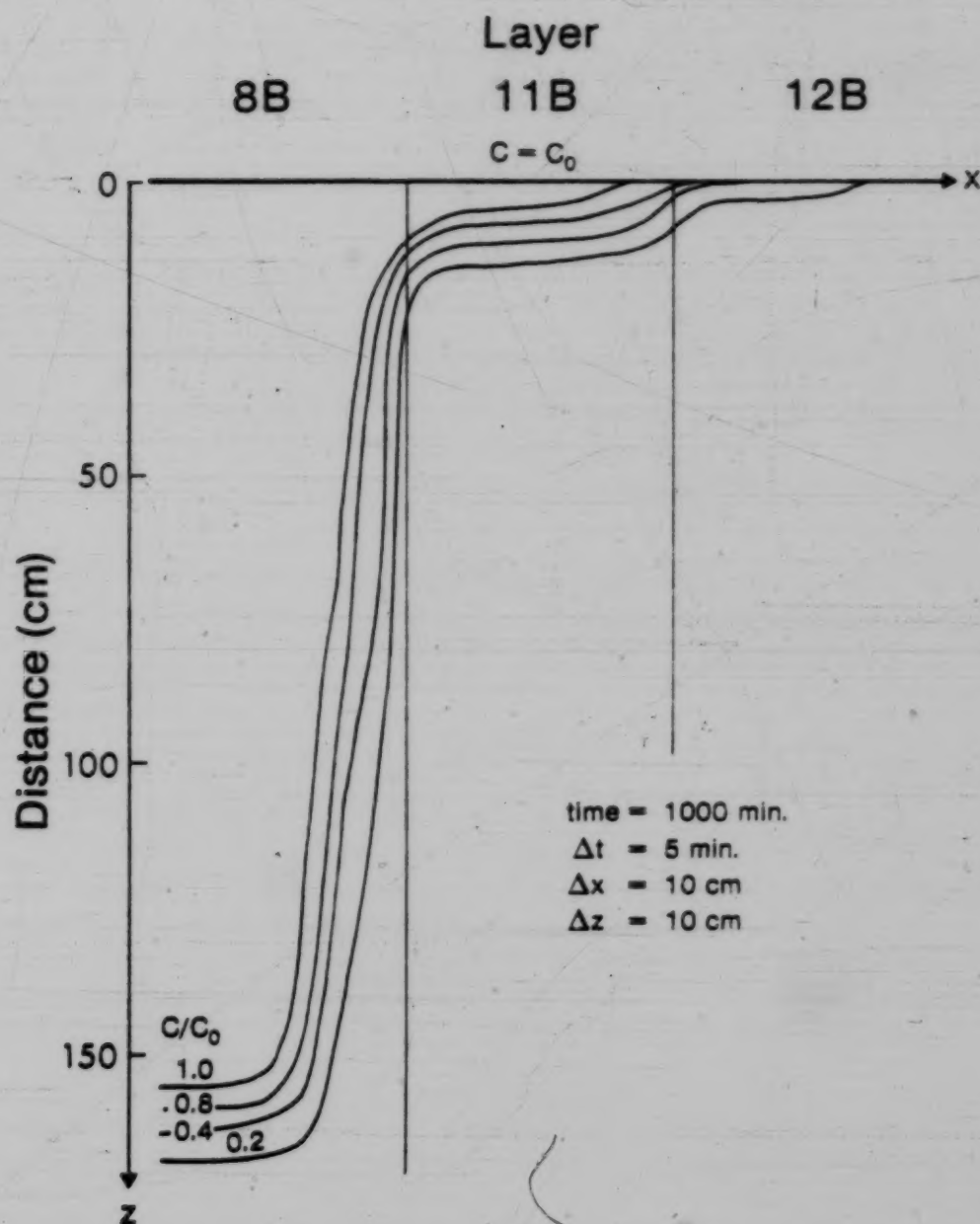


Figure 30. Two-dimensional Mass Transport without Ion Exchange in a Three-layered Medium, 8B/11B/12B

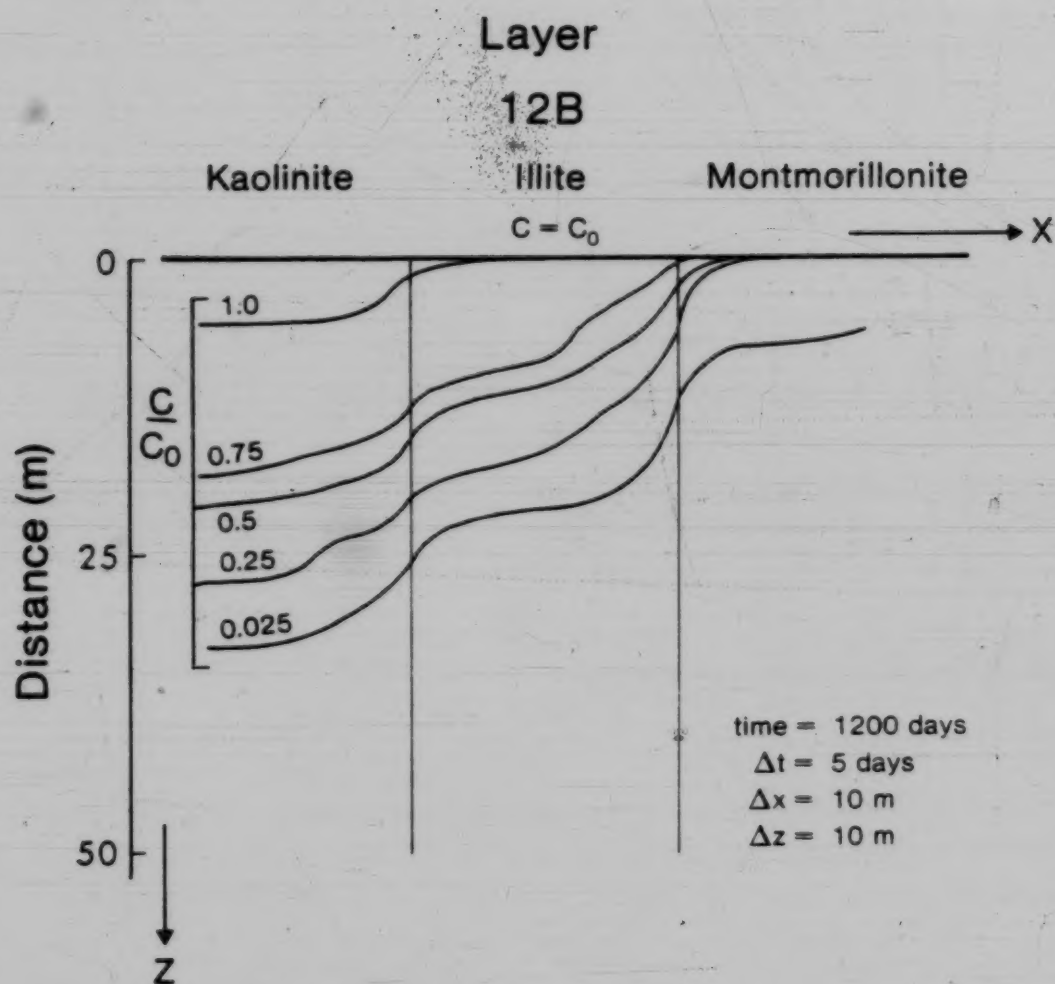


Figure 31. Effect of Individual Clays on Two-dimensional Mass Transport in a Three-layered Medium

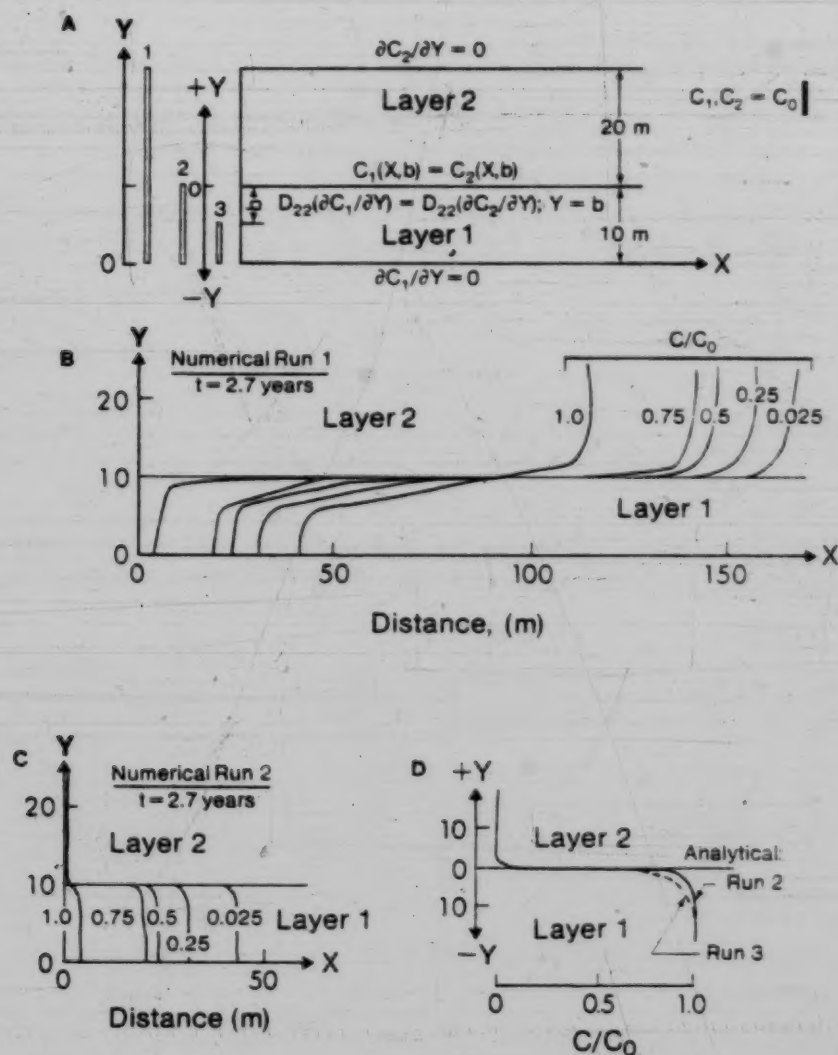
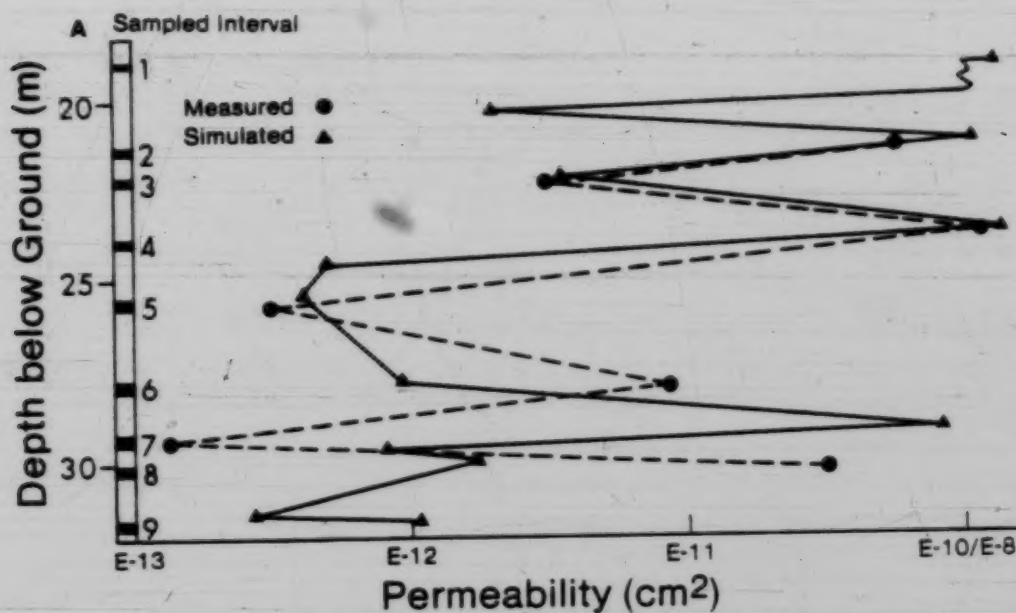
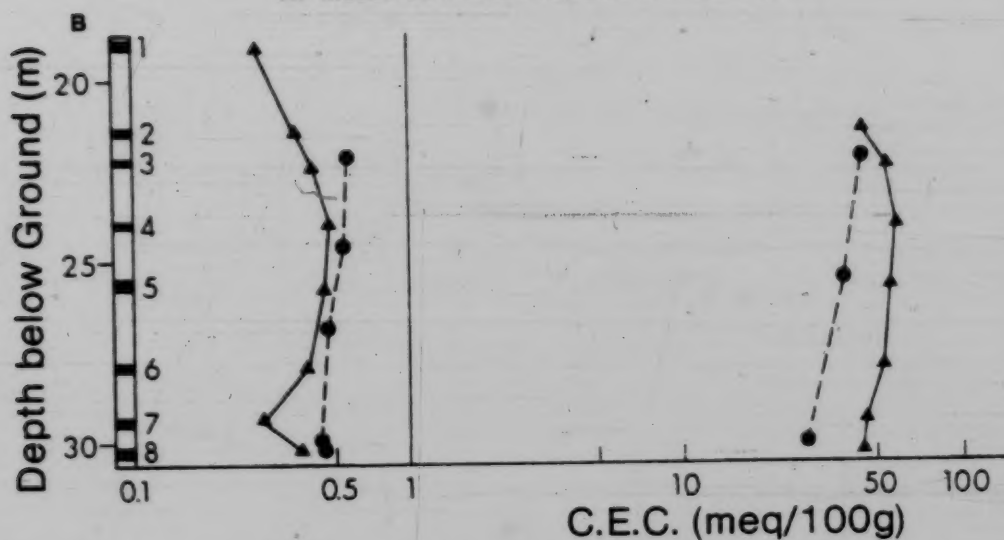


Figure 32. Numerical and Analytical Solutions of Two-dimensional Mass Transport in a Two-layered Geological Medium:

- A. Boundary and Initial Conditions of the Analytical Solution (Analytical Runs 2 and 3) and Starting Condition for the Numerical Solution (Numerical Runs 1 and 2)
- B. Mass Transport in the Milk River System, Run 1
- C. Mass Transport in the Milk River System, Run 2
- D. Relative Concentration Profile at Steady State

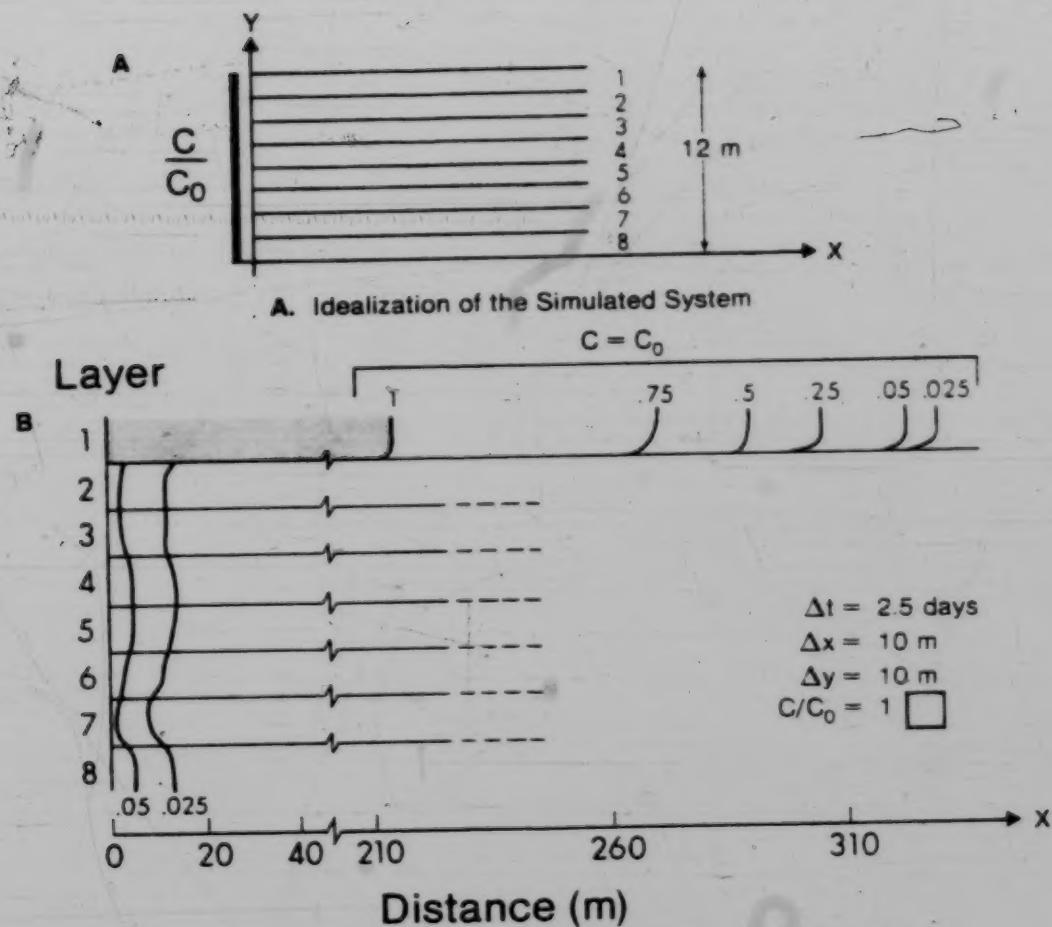


A. Measured versus Simulated Permeability



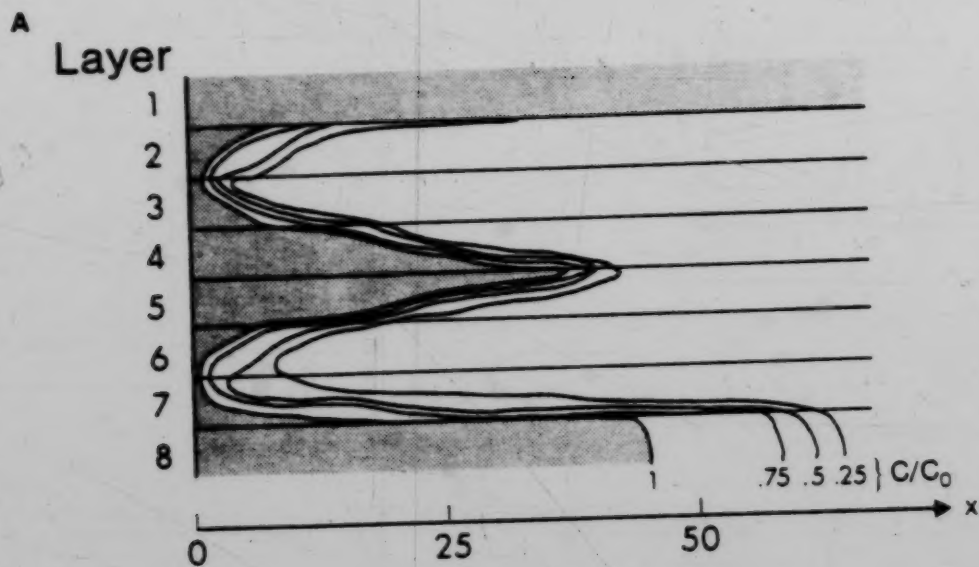
B. Measured versus Simulated Porosity and CEC

Figure 33. Comparison of the Measured and Simulated Parameters of the Oxnard Aquitard Section:

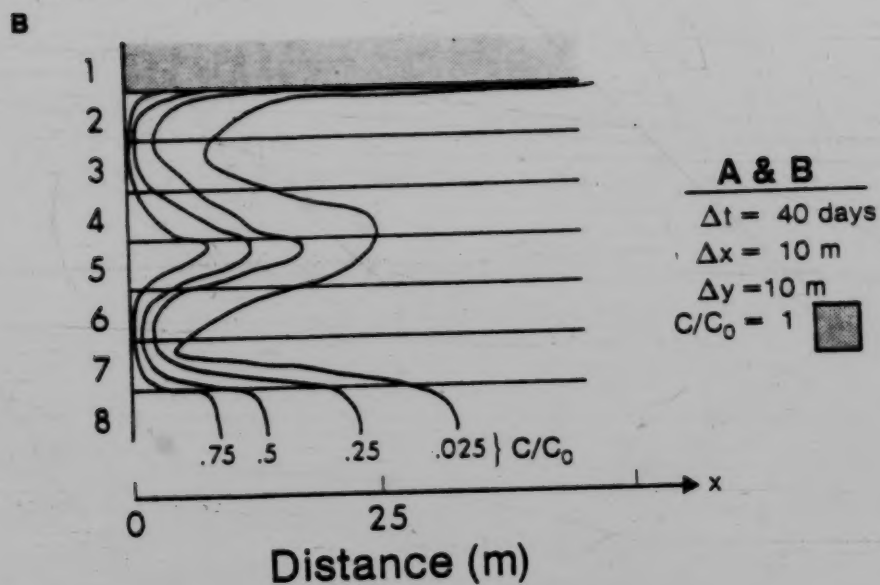


B. Mass Transport with Ion Exchange within the Idealized System

Figure 34. Simulation of Mass Transport in the Oxnard Aquitard Section at a Time of 100 Days:



A. Mass Transport without Ion Exchange



B. Mass Transport with Ion Exchange

Figure 35. Simulation of Mass Transport in the Oxnard Aquitard Section at a Time of 9600 Days:

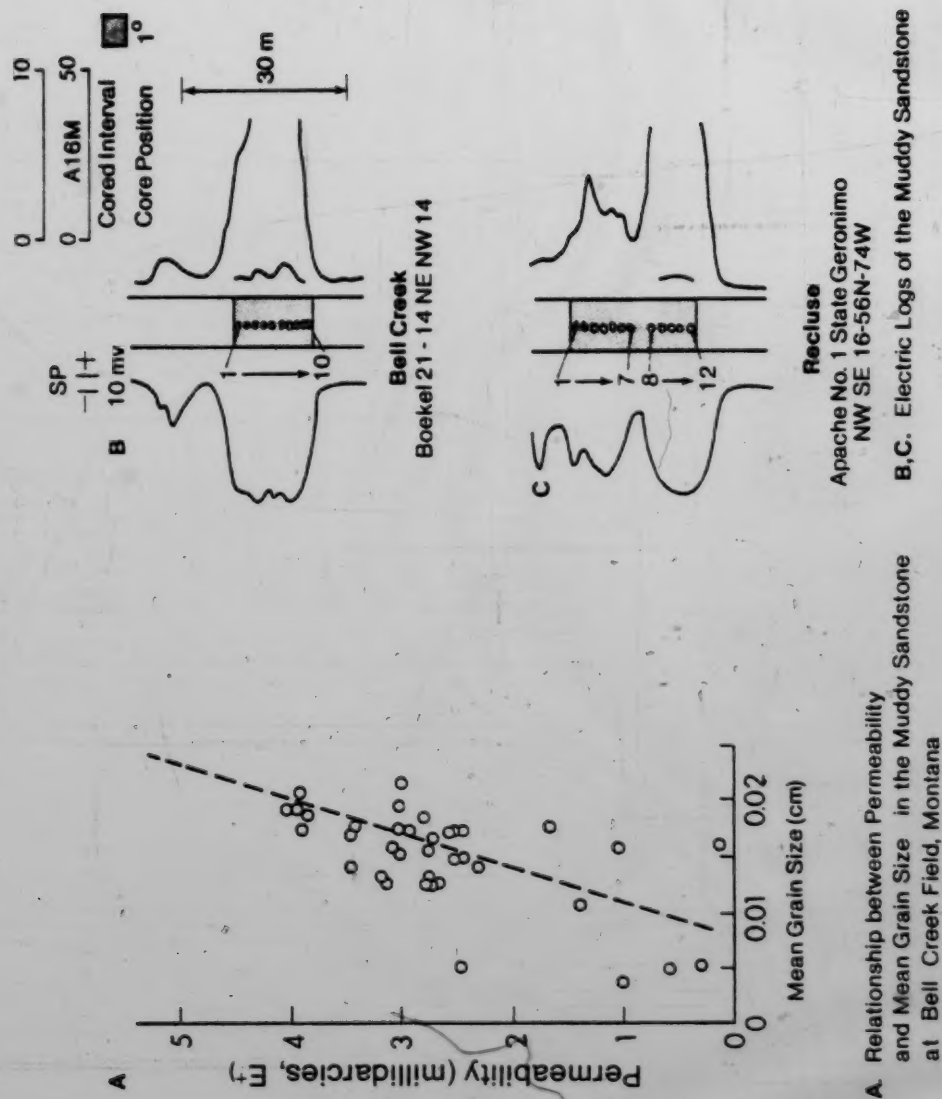


Figure 36. Permeability, Mean Grain Size and Sampled Interval Electric Logs of the Muddy Formation

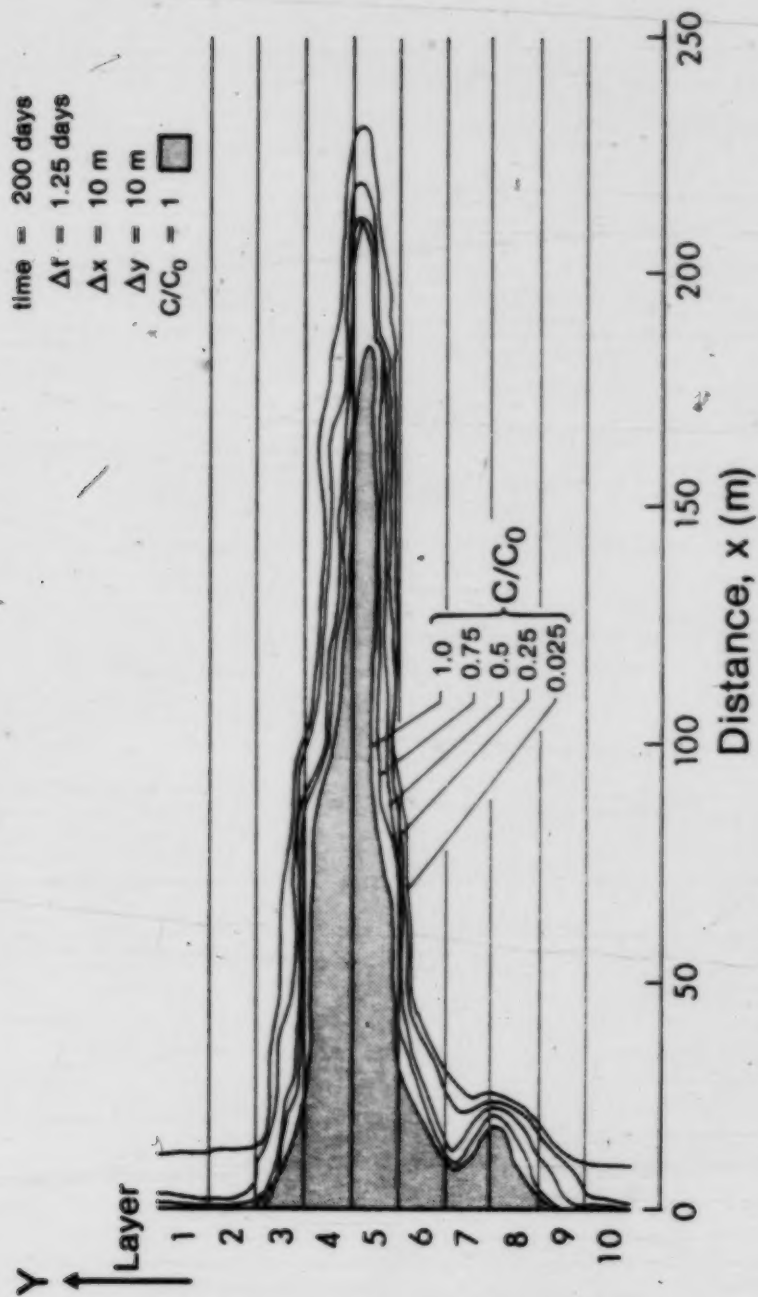


Figure 37. Simulation of Mass Transport in Section A2 of the Muddy Sandstone

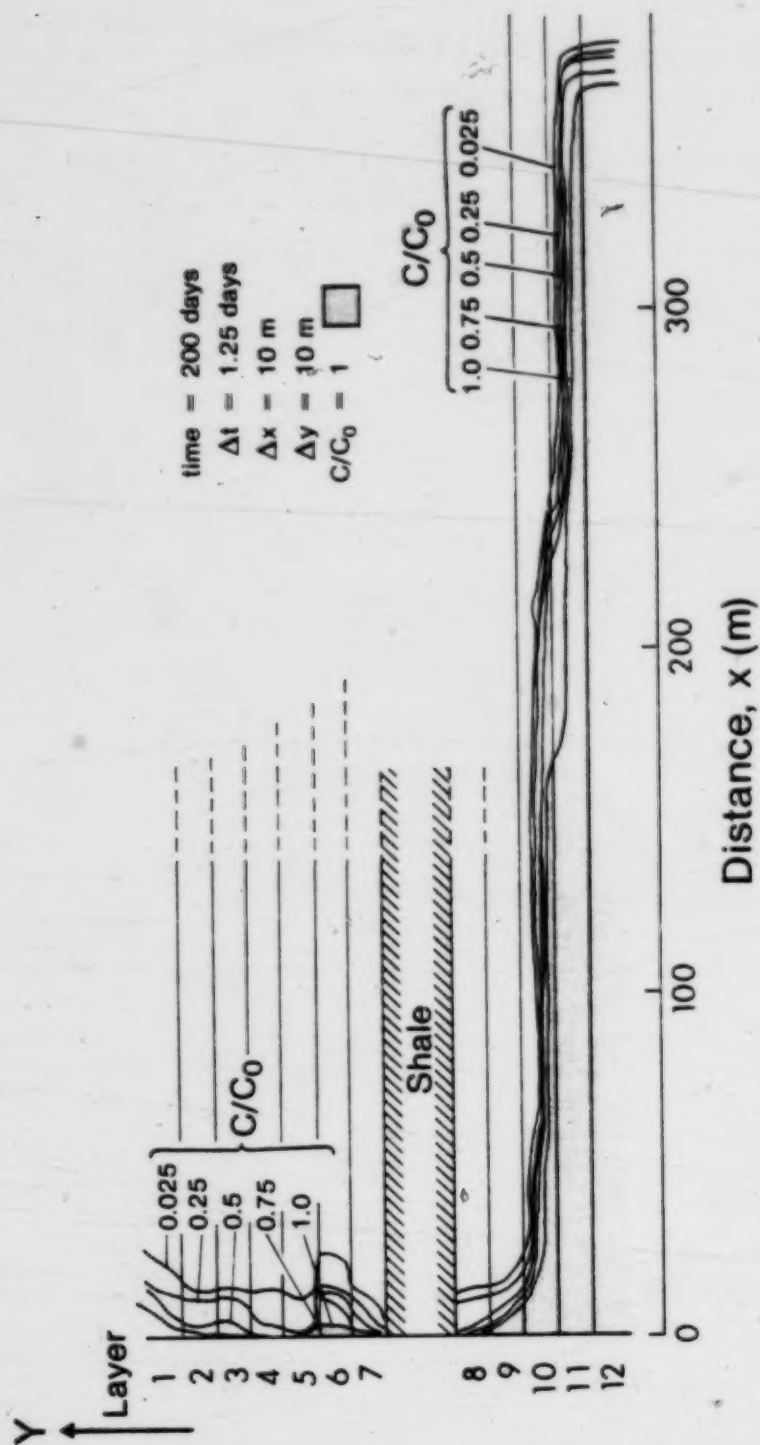


Figure 38. Simulation of Mass Transport in Section B4 of the Muddy Sandstone

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APPENDIX 1 - DESCRIPTION, TABULATION AND ANALYSIS OF PRIMARY DATA SETS

Summary Descriptions of Primary Data Sets.

Five Data Sets are used to illustrate the procedures developed in this work for the determination of the model parameters. Data Sets illustrative of the interrelationship of textural and transport characteristics of clastic sediments are chosen because they include measurements of porosity, permeability and grain size distributions. Also included are some mineralogic data together with background information on the geology of the samples. Where possible, I experimentally determined the specific surface and CEC to complement the published or tabulated information. Similar considerations apply to the Data Sets comprising samples of clastic sandstones, but more importance was attached to obtaining published data on the clay mineral content of the samples.

The data obtained by Klotz et al. (1980) are included in the primary Data Sets because they are a synthesis of extensive laboratory and field measurements of grain size parameters and dispersion in unconsolidated alluvial and fluvio-glacial sediments. These data are listed in Appendix 2 together with the other data on longitudinal and transverse dispersion. A search of the literature for studies relating textural, mineralogic and transport parameters for clay-rich sandstones failed to discover any

significant reports, and it is necessary to use the more restricted sets of data listed in Appendix 2.

Summary descriptions and some background information about the primary Data Sets are provided below:

Data Set 1 - Erin and Morne L'Enfer Formations, Southern Trinidad, West Indies.

Lithological descriptions and analyses of grain size distribution, porosity and bulk density of sidewall cores from Trinidad Tesoro Petroleum Company wells PS 926W and PS 946W; sidewall cores from Water and Sewerage Authority wells 2173 Erin and Coora 10. These last two sample sets consist of a few grams of material from the sidewall core, on which the specific surface and CEC were measured in the course of the present study. The lithology and grain size distributions of sidewall cores from PS 926W and PS 946W are listed in Tables A1.1.1 through A1.1.3; data from Coora 10 and 2173 Erin are tabulated in Table A1.1.4.

The Erin and Morne L'Enfer Formations occur over a wide area of southwestern Trinidad, West Indies. They consist of sands with varying quantities of interbedded and interstitial silt, clay and lignitic material. Suter (1960) provides an overview of the stratigraphy and structure of the formations and Bower (1968), Saunders and Kennedy (1968) and Milne-Home (1979) discuss various aspects of the sedimentology of the Morne L'Enfer Formation.

TABLE A1.1.1. DESCRIPTION OF SIDEWALL CORES, PS-926W
AND PS-946W

Sample Depth (ft)	Permea- bility (cm ²)	Porosity	Bulk Density (g/cm ³)	Lithology

PS - 926W				
131	4.56E-9	.322	2.07	m gr sd w ln str
250	2.09E-9	.347	2.29	m gr sd
321	6.54E-9	.364	1.93	f gr sd w ln str'
350	7.27E-10	.378	2.03	f gr sd w ln str
501	2.94E-8	.281	2.05	siy f gr sd'
551	1.05E-9	.205	2.18	f gr sd
PS - 946W				
650	1.07E-9	.372	1.97	f gr sd
660	6.22E-9	.354	2.06	vf gr cly cal sd
670	9.67E-9	.265	1.95	vf gr cly cal sd w ln
689	2.91E-9	.336	2.03	vf gr cly cal sd w ln
704	1.20E-8	.367	2.00	vf gr cly cal sd w ln lam
753	2.44E-9	.369	1.98	f gr sd
775	1.97E-9	.393	1.95	vf gr cly lam sd w ln
787	1.67E-9	.362	2.10	vf gr cly lam sd w ln
885	2.83E-9	.357	2.01	vf gr xb lam siy sd
890	1.10E-8	.330	1.93	vf gr xb lam siy sd
910	8.94E-9	.315	2.06	f gr sd
920	4.14E-8	.314	2.07	f gr sd'
930	2.28E-8	.263	2.12	f gr sd
961	1.85E-8	.319	2.09	f gr sd
978	1.01E-8	.345	1.97	f gr sd
1008	7.96E-9	.271	2.11	f gr lam siy sd
1017	2.16E-8	.297	2.02	m gr sd
1020	3.79E-9	.296	2.07	m gr siy sd w ln lam
1054	4.66E-9	.317	2.05	m gr sd w tr ln

'cracked sample; sd=sand; ln=lignite; m=medium; f=fine;
v=very;
gr=grained; cly=clayey; siy=silty; lam=laminated;
xb=crossbedded; w=with;
cal=calcareous; str=streak; tr=trace.

TABLE A1.1.2. GRAIN SIZE DISTRIBUTIONS, PS 926W SAMPLES.
Fractional Composition of Sample

(Depth) Mean Size (cm)	(161)	(250)	(350)	(551)
.03834		.004	.048	.132
.02958	.022	.088	.031	.276
.02104	.225	.540	.079	.169
.01487	.327	.161	.404	.102
.01049	.213	.077	.233	.071
.00742	.080	.045	.063	.053
.00524	.053	.039	.051	.056
.00403	.007	.006	.008	.008
.00339	.013	.006	.018	.053
.00220	.025	.014	.025	.036
.00110	.022	.014	.023	.030
.00055	.009	.003	.011	.011
.00030				.002
.000096	.0039			
.000090		.0029		
.000060			.0059	

TABLE A1.1.3. GRAIN SIZE DISTRIBUTIONS, PS 946W SAMPLES.
Fractional Composition of Samples (Depth)

Mean Size (cm)	(650)	(660)	(670)	(689)	(704)	(753)	(775)	(787)	(885)	(890)
.02958	.184	.028	.013	.025	.029	.003	.061	.078	.077	.025
.02104	.219	.055	.058	.048	.041	.034	.067	.096	.066	.167
.01487	.190	.236	.232	.105	.068	.448	.125	.187	.109	.425
.01049	.127	.422	.405	.363	.168	.259	.302	.215	.285	.126
.00742	.067	.117	.144	.186	.224	.077	.126	.135	.149	.071
.00524	.076	.061	.060	.118	.227	.068	.125	.115	.153	.062
.00403	.007	.004	.010	.018	.029	.008	.017	.010	.005	.010
.00339	.060	.022	.033	.042	.094	.028	.057	.052	.051	.044
.00220	.035	.025	.026	.050	.075	.035	.060	.052	.055	.035
.00110	.028	.022	.016	.029	.042	.028	.044	.042	.034	.025
.00058					.0029					
.00055	.006	.006		.0136		.009	.0133	.0148	.014	.018
.00035			.0029							
.00022								.0019		
.00021				.0023						
.00020									.0019	
.00019		.0019				.0026				
.00017							.0031			
.00015					.0029					

TABLE A1.1.3. Continued...

Mean
Size (910) (930) (961) (978) (1008) (1017) (1020) (1054)
(cm)

.03834		.030						
.02958	.063	.258	.015	.038	.006	.126	.057	.059
.02104	.281	.285	.121	.169	.062	.418	.435	.207
.01487	.253	.131	.394	.292	.241	.123	.155	.137
.01049	.138	.080	.179	.217	.290	.083	.097	.214
.00742	.069	.054	.077	.084	.156	.059	.058	.128
.00524	.073	.052	.069	.064	.087	.068	.073	.113
.00403	.008	.010	.013	.013	.007	.009	.007	.009
.00339	.040	.038	.042	.053	.056	.049	.043	.048
.00220	.038	.029	.045	.038	.050	.033	.045	.050
.00110	.028	.024	.033	.025	.029	.024	.029	.029
.00055	.007	.0068	.0097	.006	.0054	.0065	.0085	.0054
.00036					.005			
.00035								.005
.00028				.009				
.00020	.0016					.0014		
.00020			.0022					
.00018		.0021						

TABLE A1.1.4. MEASURED PROPERTIES OF SAMPLES FROM COORA 10
AND 2173 ERIN.

Sample No.	Depth (ft.)	Specific Surface (cm ² /gm)	C. E. C. (meq/100gm)
Coora 10			
1	256	19.56	1.95
2	260	45.69	3.64
3	284	165.52	12.47
4	373	85.18	6.56
5	435	25.84	20.74
6	460	71.39	3.27
7	480	53.14	4.20
8	500	80.74	4.80
9	600	19.65	4.39
10	645	61.18	5.52
11	650	29.69	3.08
12	705	72.00	4.44
13	760	81.79	6.47
14	800	63.21	5.51
15	820	44.09	4.13
2173 Erin			
16	524	174.71	13.27
17	790	46.89	4.53
18	858	108.68	7.46
19	912	127.66	7.84
20	1060	199.07	17.73
21	1125	130.50	10.44
22	1190	81.24	7.78
23	1195	117.63	8.46

**Data Set 2 - Quaternary Alluvium, Grande Prairie, Arkansas,
U.S.A.**

Lithological descriptions, partial mineralogy, grain size distributions, porosity and permeability measurements on a suite of samples from United States Geological Survey test holes L3S-4W-3dca 14, 5S-3W-17ddd1 and 5S-2W-36abb1, (Johnson et al., 1967). These data are listed in Tables A1.1.5 through A1.1.8.

In the Grande Prairie region of Arkansas the Quaternary alluvium is divided into two zones. The Upper Zone consists of very dense silt and clay layers. The Basal zone comprises very fine to coarse sand and very fine to coarse gravel complexly interbedded with in clay and silt lenses. Cobbles and boulders are common in the lower part of the Basal Zone.

The samples are disturbed samples obtained by augering or bailing. They were air dried and the grain size distribution measured by sieve and hydrometer. The coefficient of permeability was determined in constant head and variable head permeameters. The samples were repacked for permeability, dry unit weight, relative density and porosity determinations, using the specially designed packing machine described by Morris and Johnson (1966).

TABLE A1.1.5. LITHOLOGY OF GRANDE PRAIRIE SAMPLES.

Sample Number	Lithology
58ARK55	Sd, f to m, l bl-gr, cal in part; some vf & vc sd
58ARK56	Sd, f to m, dk bl-gr, cal in part; some vf & vc sd
58ARK57	Sd, f to m, dk bl-gr, cal in part
58ARK58	Sd, f to m, l bl-gr, cal in part; si & vf to vc sd
58ARK59	Sd, f to m, l bl-gr, cal in part; some f & c sd
58ARK60	Sd, f to m, l bl-gr, cal in part; some vf & c sd
58ARK61	Sd, f to c, l bl-gr, cal in part, some vf & vc sd lenses of v cly sd; scattered cl balls & cl
58ARK62	Sd, f to m, l bl-gr, cal in part; scattered vf, c & vc sd
58ARK63	Sd, f to m, l bl-gr, cal in part; scattered vf, c & vc sd
58ARK64	Sd, m to vc, l bl-gr, cal in part; some f sd + 10% vf to m grav
58ARK65	Sd, m to vc, l bl-gr, cal in part, some f sd + 10% vf to m grav
58ARK66	Sd, m to c, l bl-gr, cal in part; some f & vc sd sd to m grav
58ARK67	Sd, m, l bl-gr, cal in part; c to vc sd + scattered vf to f grav
59ARK44	not recorded
59ARK45	not recorded

bl = blue; c = coarse; cal = calcareous; cl = clay; cly =
clayey; dk = dark;
f = fine; grav = gravel; gr = gray; l = light; m = medium;
qz = quartz; sd = sand; si = silt; sl = slightly; v = very;

TABLE A1.1.6. GRAIN SIZE DISTRIBUTIONS OF
GRANDE PRAIRIE SAMPLES.

Geom.	58	58	58	58	58	58	58	58
Mean	ARK	ARK	ARK	ARK	ARK	ARK	ARK	ARK
Size	54	55	56	57	58	59	60	61
(cm)	(Fractional composition of samples)							

.00224	.108	.134	.090	.078	.058	.053	.026	.074
.00884	.073	.113	.116	.111	.082	.118	.045	.030
.0177	.181	.286	.385	.349	.221	.239	.137	.095
.0354	.580	.434	.397	.447	.556	.501	.723	.618
.0707	.052	.032	.012	.014	.077	.088	.068	.157
.1414	.003	.001			.001	.001	.001	.015
.283					.005			.015
.566								.011

TABLE A1.1.6. Continued...

Geom.	58	58	58	58	58	58	59	59
Mean	ARK	ARK	ARK	ARK	ARK	ARK	ARK	ARK
Size	62	63	64	65	66	67	44	45
(cm)	(Fractional composition of samples)							

.00039							.065	.113
.00224	.015	.007		.002			.145	.333
.00884	.009	.007	.001	.007	.001	.004	.460	.498
.0177	.201	.332	.105	.099	.079	.095	.326	.051
.0354	.676	.590	.322	.375	.642	.677	.002	.001
.0707	.095	.049	.359	.317	.214	.182		.002
.1414	.004	.010	.096	.086	.028	.018	.002	.002
.283		.005	.027	.052	.013	.006		
.566			.017	.036	.012	.011		
1.131			.033	.026	.011	.003		
2.263			.040					

TABLE A1.1.7. UNIFORMITY COEFFICIENT, POROSITY AND PERMEABILITY OF THE GRANDE PRAIRIE SAMPLES.

Sample No.	UC	Porosity	Permeability (cm ²)
58ARK54	5.33	.328	1.63E-8
58ARK55	5.30	.347	1.08E-8
58ARK56	3.7	.371	2.71E-8
58ARK57	3.5	.366	2.17E-8
58ARK58	3.2	.381	4.88E-8
58ARK59	3.7	.331	3.79E-8
58ARK60	2.2	.355	1.63E-7
58ARK61	3.2	.395	3.25E-8
58ARK62	1.8	.371	1.63E-7
58ARK63	1.4	.381	2.71E-7
58ARK64	2.6	.318	3.25E-7
58ARK65	2.4	.321	4.34E-7
58ARK66	1.8	.353	5.42E-7
58ARK67	1.7	.374	4.34E-7
59ARK44	6.8	.396	4.34E-9
59ARK45	28.6	.396	1.63E-9

TABLE A1.1.8. MINERALOGY OF GRANDE PRAIRIE SAMPLES.
Order of relative abundance: MAJOR, minor, (trace), (questionable?)

Sample No.	Mineralogy
58ARK55	QUARTZ, feldspar, (mica?), (montmorillonite?)
58ARK56	QUARTZ, feldspar, (montmorillonite), (mica), (kaolinite)
58ARK61 (kaolinite),	QUARTZ, (feldspar), (mica), (montmorillonite?)

Averaged composition of representative samples of the Upper

Quaternary clay and silt from a roadcut:

- 1) abundant feldspar with orthoclase more common than plagioclase;
- 2) moderate amounts of quartz;
- 3) clay minerals: MONTMORILLONITE, Illite, poorly crystallized kaolinite.

Data Set 3 - Data tabulated or graphed by Klotz et al. (1980).

These data result from 4300 laboratory tests and 20 field tests of dispersion in Tertiary alluvial sands and gravels from Bavaria, Quaternary aeolian and fluvial sands from northern Germany and fluvio- glacial gravels from Bavaria. The information is given by Klotz et al. (1980) as derived parameters of grain size distribution curves and as porosity and measured dispersion parameters. Data are provided also in the form of plots of longitudinal dispersion coefficients against flow velocity of the tracer solution.

Data Set 4 - Lea Park and Milk River Formations of Southern Alberta.

Lithologic descriptions and clay mineralogy of plugs from cores of the Alderson Member of the Lea Park Formation, and the Virgelle Member of the Milk River Formation, Milk River Gas Pool, Alberta, (Longstaffe, 1984). As part of the present study, experimental determinations of specific surface and CEC were made on crushed whole- rock samples from the plugs.

The Milk River Formation in the outcrop area of NW 1/4 Section 23, Township 1, Range 13, West of the 4th Meridian, according to Meyboom (1960), consists of fine- to very fine-grained, well- sorted subgreywackes. The mineral composition is 60% quartz, 10% chert, 5% weathered feldspar and

micaceous minerals with 25% matrix. The matrix consists of argillaceous material, in part poorly cemented. The sandstone is friable to poorly - cemented. The associated shale ranges in composition and texture from argillaceous sand to pure clay. The grain size distribution of the "typical" Milk River Sandstone and underlying Shale are included in Table A3.2.5 as a sample of output from GENPAR1.

TABLE A1.1.9. CLAY MINERALOGY¹, MILK RIVER AND LEA PARK FORMATIONS.

Sample	Normalized Clay Fraction (2 μ m - .2 μ m)				
	Specific Surface m ² /g	Kaolinite	Smectite	Illite	Chlorite

Virgelle Member, Milk River Formation					
1(6)	18.42	.60	.10	.20	.10
2(7)	43.28	.05	.50	.30	.10
3(20)	128.25	.05	.40	.50	.05
4(11)	132.52	.45	.20	.30	.05
5(12)	62.33	.15	.05	.65	.15
6(15)	101.93	.05	.05	.75	.15
7(19)	62.06	.35	.05	.55	.05
8(21)	17.57	.15	.20	.55	.10
9(25)	15.58	.70	.05	.20	.05
10(27)	52.54	.20	.15	.50	.15
Alderson Member, Lea Park Formation					
11(41)	98.65	.15	.05	.70	.10
12(78)	89.95	.15	t	.75	.10
13(79)	86.65	.20	t	.75	.05
14(80)	93.76	.20	t	.75	.05
15(54)	68.82	.25	.05	.60	.10
16(52)	68.66	.30	.15	.50	.05
17(62)	104.04	.20	.05	.70	.05
18(63)	18.61	.10	.05	.80	.05
19(64)	144.87	.10	.05	.75	.10
20(66)	36.09	.15	.05	.70	.10
21(65)	113.44	.15	.05	.75	.05
22(67)	72.33	.20		.70	.10
23(69)	86.00	.20	.05	.70	.05
24(70)	90.33	.15	.05	.75	.05
25(71)	78.45	.15	.05	.75	.05
26(72)	90.34	.20	.05	.70	.05
27(74)	93.23	.15	.05	.75	.05

¹Mineralogy from Longstaffe (1984);

Sample () = sample number in Longstaffe (1984);

t = trace.

Data Set 5 - Belly River Formation, Alberta.

Lithologic and petrographic descriptions and mineralogy of slabbed cores and thin sections of Basal Belly River Sandstone, Pembina Field, Alberta, supplemented with measurements of porosity and permeability by Core Laboratories Inc., (Iwuagwu, 1979; Iwuagwu and Lerbekmo, 1980). Iwuagwu (1979) describes the lithology of the Basal Belly River Sandstone as mainly fine - to medium - grained, poorly to moderately sorted, occasionally pebbly sandstone. There are minor amounts of mudstone and siltstone with carbonaceous and bentonitic shale. Detailed logs of cores from which the samples were taken are also presented by Iwuagwu (1979).

The Basal Belly River Sandstones have undergone diagenesis which has resulted in the formation of a suite of authigenic minerals within the pore space. Iwuagwu (1979) notes the presence of calcite, quartz, chert overgrowths, iron oxides and authigenic clays. Of the non - clay minerals, calcite is usually the most abundant, occurring as a microcrystalline matrix; pore - filling quartz and chert are found as well developed crystal intergrowths and the iron - oxide occurs mostly as coatings on the quartz and chert. Iwuagwu (1979) used XRD and SEM to identify the authigenic clays as well - crystallised kaolinite, fan - like rosettes of chlorite and irregular flakes of illite - montmorillonite. Kaolinite is the most abundant clay mineral and forms pore - filling, euhedral, pseudo-hexagonal booklets

made up of a series of hexagonal plates. These plates range in width from 2μ to 6μ , in length from 6μ to 10μ and are between 0.3μ and 1.0μ thick. The length of the booklets can be up to 22μ , (Iwuagwu, 1979). The random orientation of the booklets within the pore result in a bulking of 50% by volume, giving rise to considerable microporosity.

TABLE A1.1.10. BELLY RIVER SANDSTONE: POROSITY, PERMEABILITY, MEAN GRAIN SIZE AND MINERALOGY.

Sample No.	Core	Porosity T.S.	Mean Grain Size (cm)	Normalized Rock Composition						Qzd	Fsp	RF	Cement				Qza	Kaol
				Grains	Grains	Grains	Grains	Grains	Grains				Cal	FeOx	Qza	Kaol		
8		.194	.194	.036	.244	.067	.651	.001							.007	.030		
9		.176	.057	.029	.234	.119	.589								.007	.058		
10		.114	.003	.029	.223	.115	.532	.060							.002	.068		
11		.176	.050	.029	.239	.159	.521	.002							.003	.076		
12		.152	.080	.025	.212	.130	.595								.002	.061		
13		.127	.005	.030	.227	.127	.550	.014							.002	.080		
14		.048	.010	.041	.125	.076	.508	.282								.009		
15		.197	.117	.033	.237	.075	.636		.003						.003	.046		
16		.108	.025	.036	.209	.086	.467	.181								.057		
17		.233	.133	.036	.255	.083	.601	.002	.002						.015	.042		
18		.180	.052	.032	.249	.054	.631								.007	.059		
19		.166	.033	.031	.223	.080	.583	.038							.002	.074		
20		.168	.058	.031	.249	.082	.594								.005	.070		
21		.175	.093	.036	.275	.046	.615								.009	.055		
22		.169	.073	.030	.290	.039	.597	.002	.005						.007	.060		
23		.192	.065	.032	.324	.070	.549		.002						.011	.044		
24		.178	.033	.029	.192	.092	.644		.005						.005	.062		
25		.150	.038	.029	.239	.115	.564	.002								.080		
26		.155	.008	.036	.252	.102	.525	.063	.005						.005	.048		
27		.148	.022	.030	.235	.113	.543		.015						.007	.087		
28		.094	.027	.023	.220	.148	.556	.016								.060		
29		.196	.067	.032	.294	.047	.606								.003	.050		
30		.224	.103	.035	.250	.059	.637								.007	.047		

T.S. = thin section; md = millidarcies;

Mineralogy:

Qzd = detrital quartz; Fsp = feldspar; RF = rock fragments;

Cal = calcite; FeOx = iron oxides; Qza = authigenic quartz;

kaol = kaolinite.

Estimation of Shape Coefficients for the Determination of Permeability

The application of (16) to the determination of the specific surface term in (12) for the calculation of permeability is demonstrated using PS 946W - 689 as an example. The cumulative weight percentage retained on the various sieve sizes is plotted on log-probability paper against the geometric mean of adjacent sieve sizes with the data abstracted from Table A1.2.1. Cumulative percentages which approximate to a lognormal distribution plot as a straight line on this type of paper and mixtures consisting of more than one lognormal distribution plot as a series of straight line segments, (Irani and Callis, 1963). The plot for PS 946W 689, shown on Figure A1.2.1, can be fitted by two straight line segments, suggesting that the data represent a mixture of two lognormal distributions, (Harding, 1949; Bhattacharya, 1967).

One source of uncertainty in the estimation of the specific surface of the clay-sized material in the sample is that its mean grain size is smaller than the smallest sieve size. Thus, unless a hydrometer or other analysis of the size distribution of the clay-sized material is carried out separately, these fractions are lumped together and described as the "pan fraction" or "percentage smaller than the finest sieve". If, however, it is assumed that the silt- and clay-sized material also follows a lognormal distribution, then the trend of the finest measured

fractions plotted on the log- probability paper may be extrapolated to 99.99%. Hence, the mean grain sizes of the clay- sized fractions may be read from the extrapolated curve. This extrapolation for PS 946W - 689 is shown on Figure A1.2.1 and the values of mean grain size and cumulative percentages are given in Table A1.2.1.

The technique gives acceptable results for Data Sets 1 and 2, but it is arbitrary and cannot replace actual measurements. In principle it is similar to the linear extrapolation used by Folk(1966) for data in phi units, and the logarithmic extrapolation of Jaquet and Vernet (1976), except that they allocate the distribution of material down to an arbitrary lower limit of 14ϕ (6E-5mm).

The actual samples from PS 946W were not available for inspection but values of the shape coefficient, α/α_0 , were assigned to the sand, silt and clay fractions on the basis of the values for the various shapes and minerals listed in Chapter 2. From descriptions of the petrology of the Morne L'Enfer Formation, (Suter, 1960; Saunders and Kennedy, 1968), and observations on the samples from Coora 10, a reasonable estimate of the shape coefficient for the sand fraction is 9, based on the preponderance of angular quartz and minor amounts of mica and feldspar in that fraction. Assuming that the silt fractions are similarly quartz rich, a shape coefficient of 13 is assigned to the very fine silt fraction. The rationale for this is the observation by Krinsley and Smalley (1973) that silt sized quartz grains

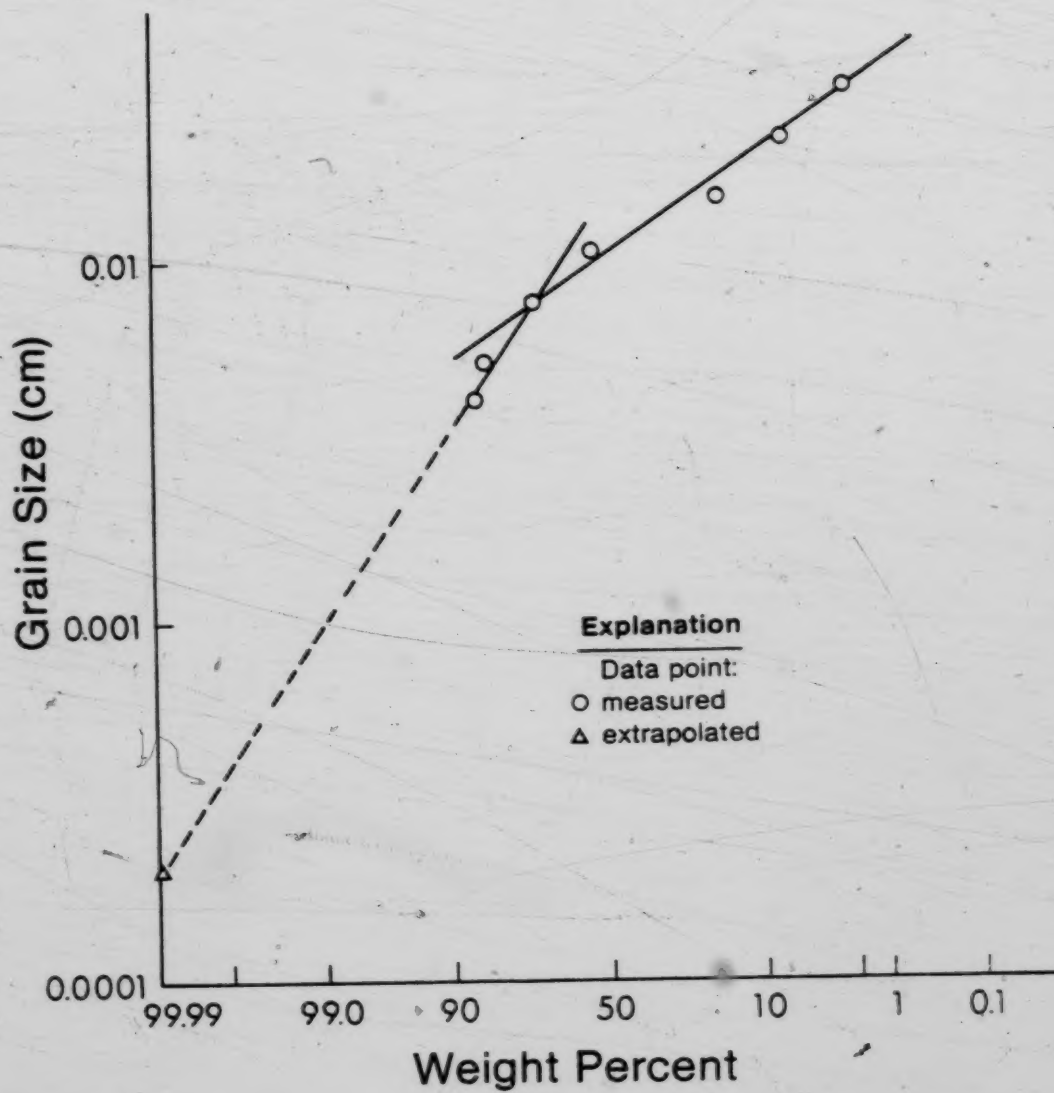


Figure A1.2.1. Grain Size Distribution, PS 946W 689

have a plate-like shape. Thus, an irregular cuboid would be a reasonable approximation for a particle in this size range. Finally, the predominance of illite and montmorillonite in these sediments suggests a shape coefficient of about 50 for the clay sized fraction.

Summing the specific surface of each size fraction, as performed in Table A1.2.1, we obtain a value of $2.31\text{E}3 \text{ cm}^{-1}$ for the total specific surface of the sample. Using the measured porosity of .336, the permeability is computed with (12) as

$$k = .0379 / (5 \times .441 \times 5.32\text{E}6) = 3.23\text{E}-9 \text{ cm}^2$$

or 326 millidarcies, compared to the measured value of 294 millidarcies ($2.91\text{E}-9 \text{ cm}^2$).

A similar computation of specific surface is shown in Table A1.2.2 for Sample 58ARK54 of Data Set 2. In this case there is no clay-sized fraction and a log-probability plot is not required. In the Grande Prairie samples quartz, feldspar, mica and kaolinite are the predominant minerals. Thus 9 and 16 are assigned as shape coefficients to the sand- and silt-sized fractions respectively. The total specific surface is computed to be 947.5 cm^{-1} and the permeability is calculated as $1.74\text{E}-8 \text{ cm}^2$, compared to a measured value of $1.63\text{E}-8 \text{ cm}^2$.

TABLE A1.2.1. WORKSHEET FOR CALCULATING SPECIFIC SURFACE
OF PS 946W - 689 .

Fraction i	G_i	D_i	G_i/D_i	$S_{o,i}$
1	.025	.02958	.845	7.606
2	.048	.02104	2.281	20.532
3	.105	.01487	7.061	63.551
4	.363	.01409	34.604	311.439
5	.186	.00742	25.067	225.606
6	.118	.00524	22.519	202.672
7	.018	.00403	44.467	40.199
8	.042	.00339	12.389	111.504
9	.050	.00220	22.727	204.545
10	.029	.00110	26.364	237.273
11	.0136	.00055	24.727	321.455
12	.0023	.00021	11.220	560.976

$$\sum S_{o,i} = S_o = 2307.358 \text{ cm}^{-1}$$

D_i = geometric mean grain size of fraction i ;

$$S_{o,i} = (G_i/D_i) \times SF$$

$$G_i = (w_i/W)/D_i;$$

w_i = weight of size fraction;

W = total weight of sample;

$G_{cum,i}$ = cumulative G_i ;

SF = shape coefficient: SF of G_1 to $G_{10} = 9$; $G_{11} = 13$;

$$G_{12} = 50.$$

TABLE A1.2.2. WORKSHEET FOR CALCULATING SPECIFIC SURFACE
OF 58ARK54.

Fraction i	G_i	D_i	G_i/D_i	$S_{o,i}$
1	.003	.283	.0106	.0954
2	.003	.1414	.0212	.1908
3	.052	.0707	.7355	6.6195
4	.580	.0354	16.384	147.456
5	.181	.0177	10.226	92.034
6	.073	.00884	8.258	74.322
7	.108	.00224	48.214	626.782

$$\sum S_{o,i} = S_o = 947.4997 \text{ cm}^{-1}$$

$i = 1$ to 6 , SF = 9; $i = 7$, SF = 16.

In order to determine the specific surface of a sandstone, the specific surface of each of the constituent minerals is obtained from Table 4 or similar compendia; this value is weighted by the proportional concentration of the mineral. Similar results may be obtained also from purely geometrical considerations if there is sufficient information on dimensions and shapes of the mineral particles.

An example of this technique is provided by kaolinite in the Belly River Sandstone. Using the the dimensions of kaolinite plates and booklets given by Iwuagwu (1979), the size of an average booklet is $20\mu \times 8\mu \times 4\mu$, yielding a volume of $6.4E-10 \text{ cm}^3$ and a surface area of $5.44E-6 \text{ cm}^2$. With a relative density of 2.65 for kaolinite, the specific surface of the booklet becomes $.32 \text{ m}^2/\text{g}$. If one assumes that the pore chambers of the sandstone are equidimensional, and using Figure 1, a mean grain size of $.03 \text{ cm}$ gives a pore size of $.006 \text{ cm}$ and a pore volume of $2.16E-7 \text{ cm}^3$. Thus, 338 booklets would fill the pore space, and a volume equivalent of 168 booklets would give rise to the 50% porosity reported by Iwuawu (1979). Hence the total specific surface, S_m would be $54 \text{ m}^2/\text{g}$, and with the further assumption of 50% bulking due to the random orientation of the booklets, the specific surface reduces to the value of $27 \text{ m}^2/\text{g}$ used in the simulation.

Derivation of Equation 2

The data used to develop the model for prediction of porosity from grain size parameters are tabulated below. Also tabulated is an outline analysis of the regression.

TABLE A1.3.1. DATA AND ANALYSIS OF POROSITY PREDICTION MODEL.

Sample No.	U.C.	RF	RFF	Porosity Measured	Porosity Predicted
PS926W - 161	3.09	.07	308.13	.322	.346
- 250	2.30	.04	426.00	.347	.351
- 350	2.90	.07	639.00	.378	.356
- 551	6.90	.10	639.00	.378	.335
PS946W - 650	5.47	.10	109.56	.205	.323
- 660	3.00	.05	152.63	.354	.338
- 670	2.41	.06	84.51	.265	.343
- 689	3.83	.12	144.29	.336	.344
- 704	3.43	.17	51.00	.367	.355
- 753	3.19	.09	197.20	.369	.345
- 775	4.33	.15	155.68	.393	.345
- 787	4.38	.14	174.00	.362	.344
- 885	4.12	.13	134.46	.357	.343
- 890	3.86	.09	147.90	.330	.338
- 910	4.63	.10	134.46	.315	.332
- 930	5.10	.08	164.33	.314	.324
- 961	4.32	.11	147.90	.263	.337
- 978	3.90	.10	105.64	.345	.338
- 1008	3.51	.12	82.17	.271	.345
- 1017	5.11	.08	134.46	.297	.323
- 1020	5.48	.09	174.00	.296	.323
- 1054	4.59	.11	84.51	.317	.333
59ARK44	4.55	.21	362.56	.396	.362
45	3.26	.45	362.56	.396	.422
58ARK57	3.85	.08	50.50	.336	.332
54	5.33	.11	126.34	.328	.326
55	5.40	.13	63.13	.347	.329
56	3.71	.09	31.56	.371	.335
58	3.20	.06	126.34	.381	.337
59	3.67	.05	63.13	.331	.329
60	2.20	.03	63.13	.355	.338
61	3.18	.08	126.34	.395	.340
62	1.79	.02	63.13	.371	.340
63	1.40	.007	126.34	.381	.343
64	2.60	.00	256.00	.318	.335
65	2.40	.002	504.91	.321	.345
66	1.80	.00	127.94	.353	.338
67	1.72	.00	127.94	.374	.339
OXNARD-72.1	9.49	.96	4750.00	.615	.603

-98	16.00	.68	6333.33	.490	.533
-221.1	20.63	.64	4133.33	.459	.412

Analysis of Variance Test of Regression...

Total SS = 1.000

Regression SS = 0.664174

Residual SS = 0.335826

F-Ratio = 24.3920

Degrees of Freedom are: 3 37

Significance Level = 0.250340E-5

R^2 = 0.6641739

R^2 , corrected for degrees of freedom = 0.6369448

APPENDIX 2. TABULATION AND ANALYSIS OF DISPERSION AND CEC DATA

Data of Klotz et al. (1980).

The data of Klotz et al. (1980), listed in Table A2.1.1, are taken from the figures in that paper as indicated within the Table. The grain size parameters and porosity of these sediments are presented in Table A2.1.2, together with the identification of the data points plotted on Figure 6.

TABLE A2.1.1. PECKET NUMBER AND DISPERSION RATIO, KLOTZ ET AL. DATA.

Material	Seepage Velocity cm/s	Mean Gr. Size cm	Peclet Number	D_{11}/D_0
A) Artificial Sands				
Fig.1, Curve 1 (medium to coarse sand)	5E-3	.061	305	700
	1E-2	.061	610	1800
	5E-2	.061	3050	1E4
	1E-1	.061	6100	21000
	5E-1	.061	30500	140000
Fig.1, Curve 2 (coarse to v. coarse sand)	5E-3	.075	375	1200
	1E-2	.075	750	2100
	5E-2	.075	3750	12000
	1E-1	.075	7500	30000
	5E-1	.075	37500	180000
	1E-3	.075	75	290
Fig.1, Curve 3 (coarse sand)	1	.075	75000	350000
	1E-3	.16	160	600
	5E-3	.16	800	2100
	1E-2	.16	1600	4000
	5E-2	.16	8000	20000
	.1	.16	16000	45000
Fig.1, Curve 4 (gravel)	.5	.16	80000	280000
	.005	.27	1350	6000
	.01	.27	2700	8000
	.05	.27	13500	30000
	.1	.27	27000	70000
	.5	.27	135000	400000
Fig.1, Curve 5	1.0	.27	270000	800000
	.005	.63	3150	9000

	.01	.63	6300	11500
	.05	.63	31500	40000
	.1	.63	63000	90000
	.3	.63	189000	310000
<i>B) Compacted Sands</i>				
Fig.2, Curve 1	.01	.10	1000	1100
(coarse to v.	.03	.10	3000	3500
coarse sand)	.05	.10	5000	6000
	.10	.10	10000	15000
	.20	.10	20000	25000
Fig.2, Curve 2	.01	.10	1000	17000
	.03	.10	3000	4800
(coarse to v.	.05	.10	5000	9000
coarse sand)	.10	.10	10000	19000
	.20	.10	20000	36000
Fig.2, Curve 3	.01	.10	1000	4000
(fine sand to	.03	.10	3000	14000
pebbles)	.05	.10	5000	22000
	.10	.10	10000	48000
	.20	.10	20000	100000
Fig.2, Curve 4	.01	.10	1000	8000
(v. fine sand	.03	.10	3000	26000
to pebbles)	.05	.10	5000	47000
	.10	.10	10000	100000
	.20	.10	20000	210000
Fig.2, Curve 5	.01	.10	1000	36000
	.03	.10	3000	130000
	.05	.10	5000	210000
	.10	.10	10000	450000
	.20	.10	20000	1000000
<i>C) Natural Sands and Gravels</i>				
Fig.7, Curve 1	.002	.017	34	190
(Quaternary	.005	.017	85	500
aeolian sand)	.01	.017	170	1000
	.02	.017	340	2200
Fig.7, Curve 2	.002	.042	84	400
(Quaternary	.003	.042	126	600
river sand)	.005	.042	210	1100
	.01	.042	420	2200
	.02	.042	840	5000
Fig.7, Curve 3	.003	.035	105	1300
(Tertiary sands	.005	.035	175	2100
and gravels)	.01	.035	350	4300
	.02	.035	700	9000
	.05	.035	1750	25000
Fig.7, Curve 4	.003	.1	300	3700
	.005	.1	500	6300
	.01	.1	1000	14000
	.02	.1	2000	30000
	.05	.1	5000	71000
Fig.7, Curve 5	.003	.3	900	8600
	.005	.3	1500	16000
	.01	.3	3000	31000
	.02	.3	6000	68000

	.05	.3	15000	170000
Fig.7, Curve 8	5E-4	.56	280	4800
(fluvio-glacial	.001	.56	560	10000
gravels at a	.003	.56	1680	36000
field test site)	.005	.56	2800	61000
	.01	.56	5600	120000
	.02	.56	11200	250000
	.05	.56	28000	630000
	.1	.56	56000	1400000
Fig.7, Curve 9	.001	.85	850	16000
	.003	.85	2550	55000
(fluvio-glacial	.005	.85	4250	90000
gravels at a	.01	.85	8500	200000
field test site)	.02	.85	17000	400000
	.05	.85	42500	950000
	.1	.85	85000	2100000
	5E-4	.85	425	7800

 Fluid is water with various tracers:

a) radioactive tracers NH_4^+ , Br^{82} , Na^{22} , J^{131} ,

Cr-EDTA, tritium;

b) NaCl solutions;

c) fluorescent dyes, e.g. fluorescein (Uranine).

Flow column length ranged between 25 cm. and 400 cm., width of 1 cm. to 50 cm.

TABLE A2.1.2. POROSITY AND GRAIN SIZE OF DATA POINTS ON
FIGURE 6.

Source (Material)	Symbol No. on Fig.6	Porosity	Mean Grain Size (cm)	U.C.	Size Range (cm)
Fig.1, Curve 1 (m to c sand)	1	.31	.061	1.55	.04 to .07
Fig.1, Curve 2 (c to vc sand)	2	.32	.075	1.85	.05 to .15
Fig.1, Curve 4 (vc sand)	3	.34	.160	1.60	.1 to .2
Fig.1, Curve 4 (gravel)	4	.31	.270	1.30	.2 to .3
Fig.1, Curve 5 (gravel)	5	.35	.630	1.30	.5 to .7
Fig.2, Curve 1 (c to vc sand)	6	.39	.100	1.10	.09 to .112
Fig.2, Curve 2 (c to vc sand)	7	.33	.100	2.00	.05 to .2
Fig.2, Curve 3 (f sand to pebbles)	8	.31	.100	5.00	.02 to .5
Fig.2, Curve 4 (vf sand to pebbles)	9	.28	.100	10.00	.01 to 1.0
Fig.2, Curve 5 (c silt to pebbles)	10	.28	.100	20.00	.005 to 2.0
Fig.7, Curve 3 (Tertiary gravel and sand)	11	.25	.035	1.13	.032'
Fig.7, Curve 4 (Tertiary gravel and sand)	12	.26	.010	7.67	.030'
Fig.7, Curve 5	13	.25	.030	18.80	.025'

c = coarse; m = medium; f = fine; v = very;
'd₁₀ of sample, cm.

The data used to develop the relationship between the dispersivity, mean grain size and uniformity coefficient, Equation 31, are taken from Tables I and II of Klotz et al. (1980). These data and an outline analysis of the regression are listed in Table A2.1.3.

TABLE A2.1.3. DATA AND ANALYSIS OF DISPERSIVITY PREDICTION MODEL.

Mean Grain Size (cm)	Uniformity Coefficient	Measured ^B	Predicted
.061	1.55	.00396	.00412
.075	1.85	.00578	.00540
.160	1.60	.00880	.00878
.270	1.30	.01300	.01148
.630	1.30	.01670	.02193
.100	1.10	.00215	.00484
.100	2.00	.00311	.00706
.100	5.00	.00830	.01259
.100	10.00	.01630	.01950
.100	20.00	.00707	.02518
.017	1.81	.00205	.00171
.042	1.96	.00464	.00359
.035	1.13	.01010	.00221
.100	7.67	.02590	.01649
.300	18.80	.06720	.29999
.560	31.30	.44700	.14934
.850	24.40	.23500	.17551

Analysis of Variance Test of Regression...

Total SS = 1.00000

Regression SS = 0.792260

Residual SS = 0.207740

F-Ratio = 26.6960

Degrees of Freedom are: 2 14

Significance Level = 0.166893E-4

R² = 0.7922601

R², corrected for degrees of freedom = 0.7625829

Data for Figure 8

TABLE A2.2.1. DATA OF BRIGHAM ET AL. (1961).

Material	Mean Grain Size, cm	Seepage Velocity (cm/s)	Peclet Number	D_{11}/D_0
Berea Sandstone core	.0042	1.14E-4	0.15	5.2
		1.79E-7	0.41	10.8
			3.50	230.0
		9.14E-3	12.00	1010.0
Torpedo Sandstone (T-1)	.0036	2.27E-7	3.2	95.0

$D_0 = 3.2E-6 \text{ cm}^2/\text{s};$
Fluids

Displaced	Displacer
89.4% Soltrol	50% mineral oil
10.6% Carbon tetra-chlor. & 94.9% Soltrol	50% kerosene & 94.8% kerosene
5.1% Carbon tetra-chlor.	5.2% heptane

TABLE A2.2.2. PROPERTIES OF FONTAINBLEU SANDSTONE.

Block of Sandstone, No.	Length (cm)	Porosity	Permeability (darcies)
A100	97.85	.184	1.5
A80	76.85	.193	1.45
A60	60.00	.168	
A20	19.80	.160	
B100	99.00	.198	1.68
B90	89.00	.211	2.05(to air)

cross-sectional area of each column = 25 cm^2 ;
fluid is aqueous NaCl in concentrations of 2 g/l and 4 g/l;
 $D_0 = 1.35E-5 \text{ cm}^2/\text{s};$
mean grain size = .02 cm.

TABLE A2.2.3. DATA OF MARTIN (1971).
 D_{11}/D_0 Peclet Number

A100 and B100	
0.5	.006
0.6	.007
0.55	.0075
0.9	.02
0.95	.03
1.2	.04
1.4	.05
2.2	.06
3.5	.065
4.0	.08
40	.9
200	4
500	8
600	15
850	25
3000	90
5500	150
A20	
40	5
50	9.5
150	40
550	80
1000	160

Derivation of Equation 33

TABLE A2.3.1. DATA AND ANALYSIS OF DISPERSIVITY PREDICTION
MODEL FOR SANDSTONES.

Sample No.	F	n	k	$d\sigma$
BA-2	13.3	.234	40	0.475
BA-3	14.2	.218	41.6	.750
BO-1	13.9	.310	1030	.670
BO-2	9.5	.320	258	.346
BO-3	8.3	.320	1430	.250
FYX-A	13.6	.218	1008	.410
FYX-B	13.3	.252	227	.366
BE-1	15.2	.190	300	.316
BE-2	15.2	.190	267	
BE-3	15.2	.190	228	.232
3501	27.6	.125	61.4	1.87
3514	41.6	.121	4.45	1.44

Source: Legatski and Katz (1967);

F = formation factor; n = porosity; k = permeability (md);

 $d\sigma$ = characteristic length.

3501 & 3514 are dolomites.

Analysis of Variance Test of Regression...

Total SS = 1.00000

Regression SS = 0.673810

Residual SS = 0.326190

F-Ratio = 4.81996

Degrees of freedom are: 3 7

Significance level = 0.398396E-1

 R^2 = 0.6738101 R^2 , corrected for degrees of freedom = 0.5340145

Data of Gibb and Cartwright (1982)

TABLE A2.4.1. GRAIN SIZE DISTRIBUTION AND MINERALOGY OF GIBB AND CARTWRIGHT SAMPLES.

S a m p l e s

Constit- 2-A4 2-A21 2-A56 3-B7 3-B9
uent+

Till

A) Grain Size Distribution (fraction)

Gravel	.01	.05	.02	.01	.01
Sand	.06	.41	.25	.45	.48
Silt	.56	.33	.38	.25	.27
Clay	.37	.21	.35	.29	.24

B) Normalized Clay Mineral Concentration

Ill-Mt	.84	.29	.60	.94	.93
Ill	.11	.54	.28	.04	.04
Chl-Kl	.05	.17	.12	.03	.03

C) pH and CEC

pH	6.3	7.4	7.5	7.0	6.9
CEC	9.2	7.4	5.4	8.4	7.7

2-A4 = Peoria Loess;

2-A21 = Glassford Till;

2-A56 = Lierle Clay;

3-B7, 3-B9 = Berry Clay.

Ill-Mt = illite/montmorillonite; Ill = illite;

Chl-Kl = chlorite/kaolinite.

Units of CEC are meq/100g.

APPENDIX 3. CODE LISTINGS AND APPLICATIONS OF GENPAR1 AND GENPAR2

Definition of Variables, Listings and Flowcharts.

The logic and operation of GENPAR1 and GENPAR2 have been described previously in Chapter 3. The variables are defined in Tables A3.1.1 and A3.1.2 and the schematic flow charts of the programs are shown in Figures A3.1.1 and A3.1.2. Listings of the codes are given in Tables A3.1.3 and A3.1.4.

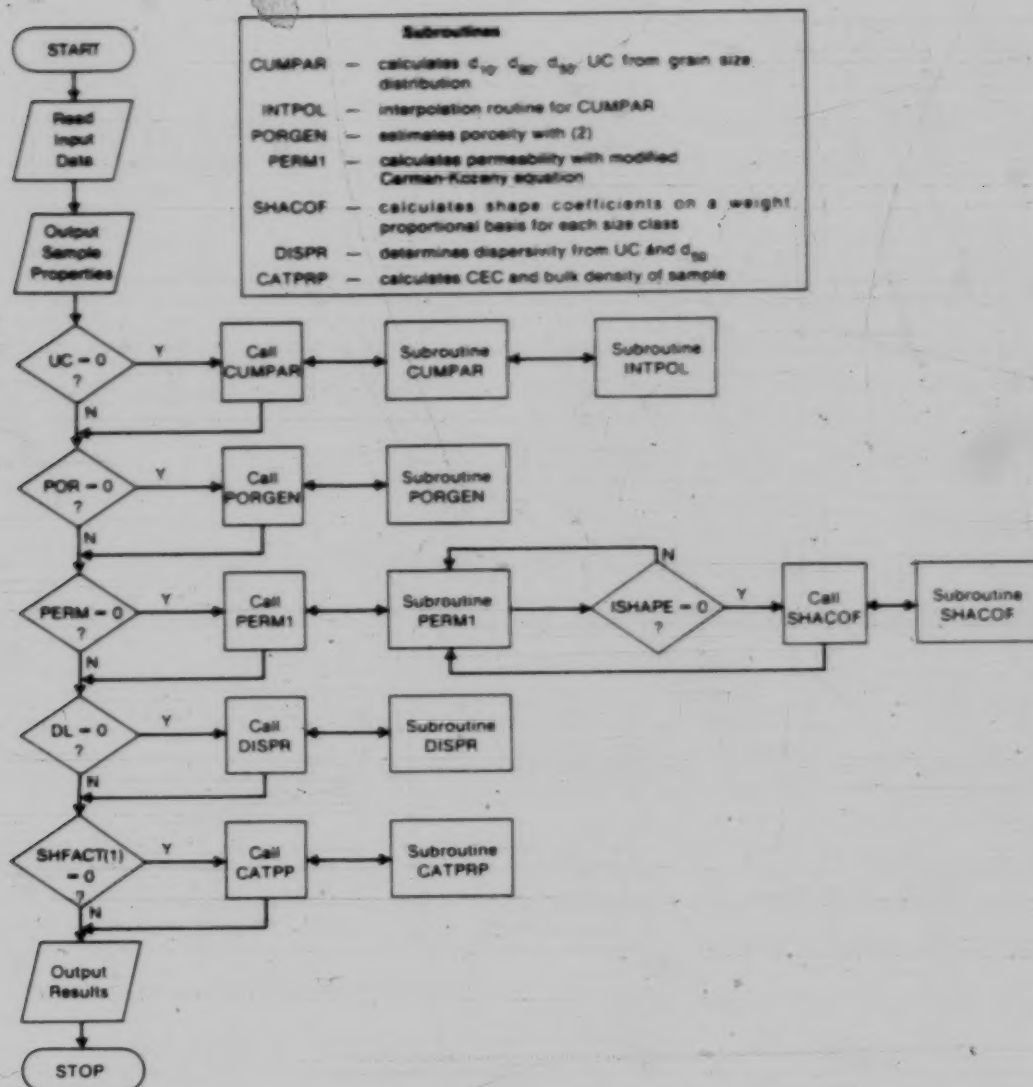
TABLE A3.1.1. DEFINITION OF VARIABLES, GENPAR1

Variable	Definition
BULK	Bulk density of sample
CATEC(I)	CEC of mineral i
CLAY	Maximum grain size of clay-sized particles
D10	grain size, 10% finer than
D50	median grain size of sample
D60	grain size, 60% finer than
DL	Longitudinal dispersion coefficient (D_L)
DSP	Dispersivity of sample
DZERO	Molecular diffusion coefficient
FACTOR	Factor to adjust grain size (usually = 1)
FMU	dynamic viscosity of liquid
FRAC(I,J)	Mineral concentration i in size fraction j
G(I)	Size fraction i
GAMMA	Specific weight of liquid
GCUM(I)	Cumulative size fraction i
GRAD	Head gradient in flow direction
IP	Switch to calculate specific surface with mineral shape coefficients for each size fraction (IP=0)
ISHAPE	Switch to calculate concentration weighted values for W1, W2 and W3 (ISHAPE#0)
NCLASS	Number of size fractions
NMIN	Number of minerals
PERM	Permeability of sample
POR	Porosity of sample, fraction
PROD(I)	Dummy array containing CEC
R(I)	Mean grain size of fraction i

RF	See Equation (2)
RFF	See Equation (2)
RHO	Density of mineral
SHFACT(I)	Shape coefficient of mineral i
SILT	Maximum grain size of silt-sized particles
TITLE	Title of simulation run
TMIN	Abbreviated names of minerals
TTMIN	Names of minerals
UC	Uniformity coefficient
VEL	interstitial velocity of liquid
W1	Size fraction shape coefficient for clay-sized particles
W2	Size fraction shape coefficient for silt-sized particles
W3	Size fraction shape coefficient for sand-sized particles

TABLE A3.1.2. DEFINITION OF VARIABLES, GENPAR2

Variable	Definition
BULK	Bulk density of sample
CLAY	Percentage of clay in sample
CATEC(I)	CEC of mineral i
CATEX	Bulk CEC of sample
CO	Pore shape factor
D	Mean grain diameter
DL	Longitudinal dispersion coefficient
DSP	Dispersivity of sample
DZERO	Molecular diffusion coefficient
F	Formation factor
FMU	Dynamic viscosity of liquid
GAMMA	Specific weight of liquid
GRAD	Head gradient in the flow direction
GF	Geometric factor for calculation of shape coefficient
II	Switch for output of dispersion parameters (II = 1 or 2)
NMIN	Number of minerals
NPROP	Number of mineral properties
PE	Peclet Number
PERM	Permeability of sample
PORM	Microporosity of sample
PORMM	Macroporosity of sample
PORTOT	Total porosity of sample
PROD(I)	Dummy array for CEC
PROP(I,J)	Property i of mineral j
RHO(I)	Density of mineral i
SM(I)	Specific surface of mineral i
SS	Specific surface of sample
TITLE	Title of simulation run
TMIN	Names of minerals
VMM	Interstitial velocity of liquid



A3.1.1. Simplified Flow Chart of GENPAR 1

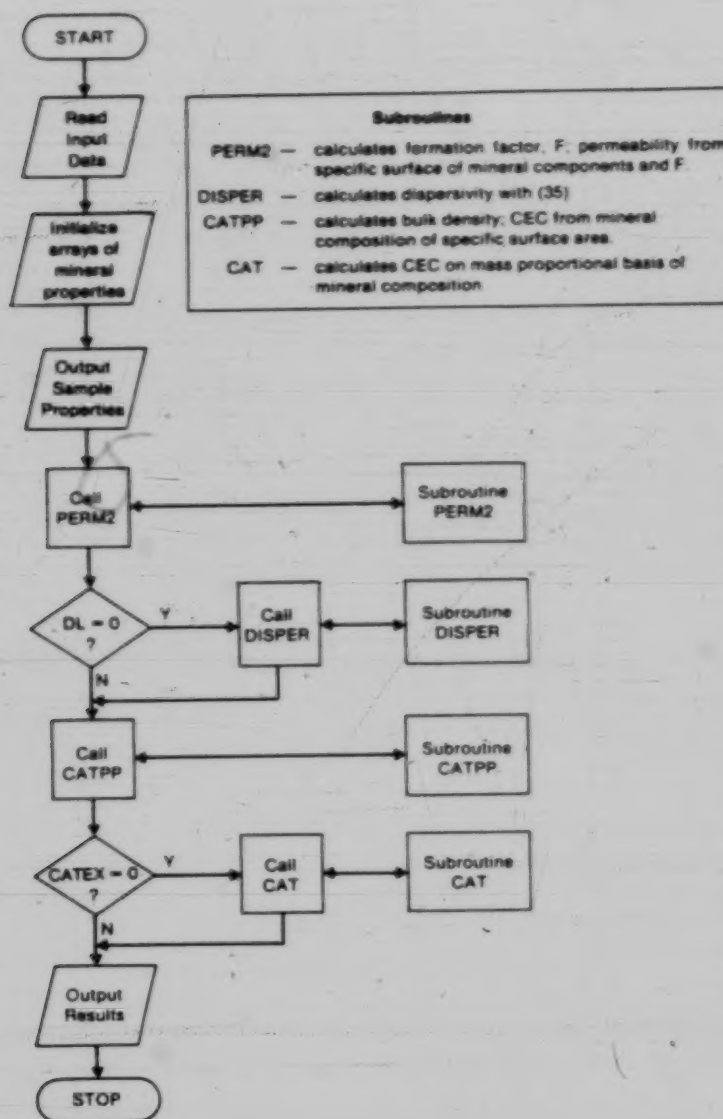


Figure A3.1.2. Simplified Flow Chart of GENPAR 2

TABLE A3.1.3. LISTING OF PROGRAM GENPAR 1

```

C      Program GENPAR1
C      to compute hydraulic and transport parameters
C      of clastic sediments from grain size distribution
C      and mineralogy.
C
C      Layout of Data File.....
C      Line 1: NDATS (15)
C      Line 2: TITLE (10A4)
C      Line 3: TMIN (10A4)
C      Line 4: NCLASS, NMIN, FACTOR (215, FS 1)
C      Line 5 et seq...R(1), I=1, NCLASS (15F6.5)
C      Line 6 et seq...G(1), I=1, NCLASS (15F6.5)
C      Line 7: UC, POR, D60, D10, D50, PERM (6F10.3)
C      Line 8: W1, W2, W3, DL, DZERO, BULK (6F10.3)
C      Line 9: SHFEACT(1), I=1, NMIN (10F5.2)
C      Line 10: RHO(1), I=1, NMIN (10F5.2)
C      Line 11: CATEC(1), I=1, NMIN (10F5.2)
C      Line 12 et seq...FRAC(I,J), I=1, NMIN; J=1, NCLASS (10F5.2)
C
C      DIMENSION R(20), G(20), GCUM(20), TITLE(20), TMIN(10), SHFEACT(10),
C      1RHO(10), CATEC(10), FRAC(20,20), PROD(10), TTMIN(20)
C      DATA GAMMA, FMU, GRAD/9.81E+2, 1.124E-2, 100.0/
C      DATA CLAY, SILT, IP, ISHAPE/ .00039, .0063, 1, 1./
C      READ(5,600)NDATS
C      DO 10 K = 1, NDATS
C      READ(5,100)TITLE
C      WRITE(6,101)TITLE
C      READ(5,700)TMIN
C      READ(5,100)TTMIN
C
C      Input grain size distribution and bulk properties
C
C      READ(5,200)NCLASS, NMIN, FACTOR
C      READ(5,300) (R(I), I=1, NCLASS)
C      DO 71 I = 1, NCLASS
C      R(I) = R(I) * FACTOR
C      71 CONTINUE
C      READ(5,300) (G(I), I=1, NCLASS)
C      READ(5,400)UC, POR, D60, D10, D50, PERM
C      READ(5,400)W1, W2, W3, DL, DZERO, BULK
C
C      Compute fines and size ratios for porosity prediction
C
C      RFF = R(1)/R(NCLASS)
C      SUM = 0.0

```

```

51 DO 41 I = 1, NCLASS
52 IF (R(I).LT..0040) SUM = SUM + G(I)
53
54 41 CONTINUE
55 RF = SUM
56
57 C
58 C Input properties of each size fraction
59 C
60 READ(5,500) (SHFACT(I), I = 1,NMIN)
61 READ(5,500) (RHO(I), I = 1,NMIN)
62 WRITE(6,2601)
63 READ(5,500) (CATEC(I), I = 1,NMIN)
64 DO 11 I = 1,NMIN
65 11 READ(5,500) (FRAC(I,J), J = 1,NCLASS)
66
67 C
68 C Output properties of sample
69 C
70 WRITE(6,301)
71 DO 21 I = 1,NCLASS
72 21 WRITE(6,401) R(I), G(I), I
73 WRITE(6,201) ITMIN
74 WRITE(6,1001)
75 WRITE(6,1101) TMIN
76 WRITE(6,1901) (RHO(I), I = 1,NMIN)
77 WRITE(6,2001) (SHFACT(I), I = 1,NMIN)
78 WRITE(6,2101) (CATEC(I), I = 1,NMIN)
79 WRITE(6,1701)
80 DO 31 J = 1,NCLASS
81 31 WRITE(6,1801) J, (FRAC(I,J), I = 1,NMIN)
82
83 SUM = 0.0
84
85 DO 51 I = 1,NCLASS
86 51 GCUM(I) = SUM + G(I)
87 SUM = GCUM(I)
88 WRITE(6,1201) RF
89 WRITE(6,1301) RFF
90 IF (W1.NE.O.) WRITE(6,1401) W1
91 IF (W2.NE.O.) WRITE(6,1501) W2
92 IF (W3.NE.O.) WRITE(6,2501) W3
93 WRITE(6,1601) DZERO
94
95 C Calculate grain size parameters, porosity, permeability,
96 C dispersivity and CEC of sample
97 C
98 IF (UC.EQ.O.) CALL CUMPAR(GCUM,R,UC,D50,D60,D10,NCLASS)
99 IF (POR.EQ.O.) CALL PORGEN(UC,R,RFF,POR)
100 IF (PERM.EQ.O.) CALL PERMI(POR,R,G,PERM,NCLASS,NMIN,W1,W2,W3,
101 1SHFACT,SS,FRAC,CLAY,SILT,IP,ISHAPE)
102 IF (DL.EQ.O.) CALL DISPR(D50,UC,PERM,POR,GRAD,GAMMA,SHFACT,DZERO,
103 1FMU,DL,NMIN,NCLASS,FRAC,B,VEL,PE)
104 WRITE(6,101) TITLE

```



```

151 1301 FORMAT(/2X,'SIZE RATIO = ',F10.3/)
152 1401 FORMAT(/2X,'PERM. SHAPE COEFF. SAND = ',F10.3/)
153 1501 FORMAT(/2X,'PERM. SHAPE COEFF. SILT = ',F10.3/)
154 1601 FORMAT(/2X,'MOLEC. DIFFUSION COEFF. = ',E14.6/)
155 1701 FORMAT(/2X,'MINERAL CONC. IN EACH SIZE FRACTION...')
156 1801 FORMAT(5X,'F5.6X,F5.2.9(4X,F5.2)')
157 1901 FORMAT(2X,'DENSITY',6X,F5.2.9(4X,F5.2))
158 2001 FORMAT(2X,'SH. FACTOR',2X,F6.2.9(3X,F6.2))
159 2101 FORMAT(2X,'C.E.C.',6X,F7.3.9(2X,F7.3))
160 2201 FORMAT(/12X,'COMPUTED PROPERTIES OF SAMPLE...')
161 2301 FORMAT(1X,'CATION EXCH. CAPACITY',3X,F10.3.2X,'MEQ/100G')
162 2401 FORMAT(/12X,'C.E.C.(MEQ/100G) DUE TO EACH EXCHANGER...')
163 2501 FORMAT(/2X,'PERM. SHAPE COEFF. CLAY = ',F10.3/)
164 2601 FORMAT(12X,'GRAIN SIZE DISTRIBUTION...')
165 2701 FORMAT(1X,'BULK DENSITY NOT CALCULATED',1X,'POROSITY',17X,F5.3)
166 2801 FORMAT(1X,'DL/DZERO',17X,F10.3)
167 STOP
168 END
169
170 C Subroutine CUMPAR
171 C
172 SUBROUTINE CUMPAR(GCUM,R,UC,D50,D60,D10,NCLASS)
173 DIMENSION R(20),GCUM(20),GCUM(20)
174 N1 = NCLASS + 1
175 GCUM(N1) = 0.0
176 N2 = NCLASS - 1
177 DO 10 I = 1, NCLASS
178 10 GCUM(I) = 1.0 - GCUM(I)
179
180 C Calculate D60
181 C
182 Z = .6
183 DO 20 I = 1, N2
184 I1 = I + 1
185 IF(GCUM(I1).GE..6.AND.GCUM(I1).LT..5)CALL INIPOL(I,I1,R,GCUM,D,Z
186 1)
187 20 CONTINUE
188 D60 = D
189
190 C Calculate D50
191 C
192 Z = .5
193 DO 30 I = 1, N2
194 I1 = I + 1
195 IF(GCUM(I1).GE..5.AND.GCUM(I1).LT..5)CALL INIPOL(I,I1,R,GCUM,D,Z
196 1)
197 30 CONTINUE
198 D50 = D
199
200 C Calculate D10

```

```

201 C
202 Z = .1
203 DO 40 I = 1, N1
204 I1 = I + 1
205 IF (CGCUM(I1).GE..1.AND.CGCUM(I1).LT..1)CALL INIPOL(I1,I1,R.CGCUM,D,Z
206 1)
207 40 CONTINUE
208 D10 = D
209 UC = D60/D10
210 RETURN
211 END
212
213 C Subroutine PORGEN
214 C
215 C
216 SUBROUTINE PORGEN(UC,RF,RFF,POR)
217 POR = .3516 - (.009571 * UC) + (.2025 * RF) + (.3102E-4 * RFF)
218 RETURN
219 END
220
221 C Subroutine PERM1
222 C
223 C
224 SUBROUTINE PERM1(POR,R,G,PERM,N,NMIN,W1,W2,W3,SHFACT,SS,FRAC,CL
225 1AY,SILT,IP,ISHAPE)
226 DIMENSION R(20), G(20), SHFACT(10), SO(20), PROD(10), FRAC(20,20)
227 POR3 = POR * POR * POR
228 PORM1 = 1. - POR
229 PORM2 = PORM1 * PORM1
230 SOTOT = 0.0
231 IF (IP.EQ.0)GO TO 1
232
233 C Calculate shape coefficients W1, W2 AND W3
234 C
235 C
236 IF (ISHAPE.NE.0)CALL SHACOF(CLAY,SILT,FRAC,SHFACT,R,W1,W2,W3,N,NMIN
237 1)
238
239 C Compute the specific surface with
240 C size-class shape coefficients W1, W2 and W3
241 C
242 CLSST = 0.
243 SISST = 0.
244 SDSST = 0.
245 DO 10 I = 1,N
246 IF (R(I).LT.CLAY)GO TO 13
247 IF (R(I).GE.CLAY.AND.R(I).LE.SILT)GO TO 12
248 IF (R(I).NE.0.)SDSS = W1 * (G(I)/R(I))
249 IF (R(I).EQ.0.)SDSS=0.
250 SDSST = SDSST + SDSS
251 GO TO 10
252 12 IF (R(I).NE.0.)SISST = W2 * (G(I)/R(I))
253 IF (R(I).EQ.0.)SISST=0.

```

```

251 SISST = SISST + SISS
252 GO TO 10
253 13 IF(R(I).NE.O.)CLSS = W3 * (G(I)/R(I))
254 IF(R(I).EQ.O.)CLSS=O.
255 CLST = CLST + CLSS
256 10 CONTINUE
257 SOTOT = CLST + SISST + SDSST
258 GO TO 11
259
260 C Compute the specific surface with mineral
261 C shape coefficients for each size fraction
262 C
263 1 DO 20 J = 1, N
264 SUM = O.O
265 DO 30 I = 1, NMIN
266 PROD(I) = SHFACT(I) * FRAC(I,J)
267 SUM = SUM + PROD(I)
268 30 CONTINUE
269 SO(J) = SUM * (G(J)/R(J))
270 SOTOT = SOTOT + SO(J)
271 20 CONTINUE
272 11 S02 = SOTOT * SOTOT
273
274 C Calculate permeability with Carman-Kozeny equation
275 C
276 PERM = POR3/(5.O * PORM2 * S02)
277 SS = SOTOT
278 RETURN
279 END
280
281 C Subroutine SHACOF
282 C
283 SUBROUTINE SHACOF(CLAY,SILT,FRAC,SHFACT,R,W1,W2,W3,N,NMIN)
284 DIMENSION R(20),SHFACT(10),FRAC(20,20),SAND(10),ASILT(10),ACLAY(10
285 1)
286 ACCCL = O.
287 ACCSI = O.
288 ACCSD = O.
289 SD = O.
290 SI = O.
291 CL = O.
292 DO 10 L = 1,N
293 IF(R(L).LT.CLAY)GO TO 2
294 IF(R(L).GT.CLAY.AND.R(1).LE.SILT)GO TO 1
295 SD = SD + 1.
296 DO 20 I = 1, NMIN
297 SAND(I) = FRAC(I,L) * SHFACT(I)
298 ACCSD = ACCSD + SAND(I)
299 20 W1 = ACCSD/SD
300 GO TO 10

```



```

301 1 SI = SI + 1.
302 DO 30 I = 1, NMIN
303   ASILT(I) = FRAC(I,L) * SHFACT(I)
304   ACCSI = ACCSI + ASILT(I)
305   W2 = ACCSI/SI
306   GO TO 10
307 2 CL = CL + 1.
308   DO 40 I = 1, NMIN
309     ACLAY(I) = FRAC(I,L) * SHFACT(I)
310     ACCCL = ACCCL + ACLAY(I)
311   W3 = ACCCL/CL
312 10 CONTINUE
313 RETURN
314 END
315
316 C Subroutine DISPR
317 C
318 C SUBROUTINE DISPR(D50,UC,PERM,POR,GRAD,GAMMA,SHFACT,DZERO,FMU,DL,
319   1HMIN,NCLASS,FRAC,B,VEL,PE)
320   DIMENSION SHFACT(10),FRAC(20,20),ACCSUM(20),PROD(10)
321
322 C Calculation of interstitial velocity
323 C
324   IF(SHFACT(1).EQ.0.)GO TO 11
325   TOTAL = 0.0
326   DO 20 J = 1, NCLASS
327     ACCSUM(J) = 0.0
328 20 CONTINUE
329   DO 10 J = 1, NCLASS
330     SUM = 0.0
331     DO 30 I = 1, NMIN
332       PROD(I) = SHFACT(I) * FRAC(I,J)
333     SUM = SUM + PROD(I)
334     ACCSUM(J) = SUM
335   TOTAL = ACCSUM(J) + TOTAL
336 10 CONTINUE
337   SFAV = TOTAL/FLOAT(NCLASS)
338   IF(SFAV.GE.9.0) GO TO 11
339   G = 1.49
340   X = 1.09
341   GO TO 21
342 11 G = 1.33
343   X = 1.28
344 21 CONTINUE
345   TAU = POR * (G * (POR**(-X)) + (1 - G))
346   VEL = (PERM/POR * SQRT(TAU)) * (GAMMA/FMU) * GRAD
347
348 C Compute Peclet Number and dispersion coeff.
349 C
350   B = .026 * (UC**.63) * (D50**.76)

```

```

351 PE = (VEL * DSO)/DZERO
352 IF(PE.GE.100) GO TO 31
353 IF(PE.LT.100.AND.PE.GT.1.) GO TO 41
354 DL = 0.67 * DZERO
355 RETURN
356
357 31 DL = B * VEL
358 RETURN
359 41 DSTAR = DZERO * ((0.5 * POR) + (0.5 * POR * POR))
360 DL = B * VEL + DSTAR
361 RETURN
362 END
363
364 C Subroutine CATPRP
365 C
366 SUBROUTINE CATPRP(G,POR,RHO,FRAC,CATEC,NCLASS,NMIN,CATEX,
367 1PROD,BULK)
368 DIMENSION RHO(10),FRAC(20,10),CATEC(10),PROP(20),CEC(20),
369 1PROD(10),ACCSUM(20),G(20)
370
371 C Calculate bulk density of sample
372 DO 80 I = 1, NMIN
373 80 PROD(I) = 0.0
374 DO 10 J = 1, NCLASS
375 ACCSUM(J) = 0.0
376 10 CONTINUE
377 DO 20 J = 1, NCLASS
378 SUM = 0.0
379 DO 70 I = 1, NMIN
380 PROD(I) = RHO(I) * FRAC(I,J) * G(J)
381 70 SUM = SUM + PROD(I)
382 ACCSUM(J) = SUM
383 TOTAL = ACCSUM(J) + TOTAL
384 20 CONTINUE
385 RHOAV = TOTAL
386 TOTAL = 0.0
387 IF(BULK.EQ.0.)BULK = RHOAV * (1. - POR)
388
389 C Calculate CEC of sample
390 C
391 CATEX = 0.0
392 DO 30 J = 1, NCLASS
393 SUM = 0.0
394 DO 40 I = 1, NMIN
395 PROD(I) = FRAC(I,J) * CATEC(I) * G(J)
396 SUM = SUM + PROD(I)
397 40 CONTINUE
398 CEC(J) = SUM
399 CATEX = CATEX + CEC(J)
400 30 CONTINUE

```

Compute CEC due to each exchanger

```

DO 50 I = 1, NMIN
  SUM = 0.0
  DO 60 J = 1, NCLASS
    PROP(J) = FRAC(I,J) * G(J) * CATEC(I)
  60 SUM = SUM + PROP(J)
  50 PROD(I) = SUM
  CONTINUE
  RETURN
END

```

```

Subroutine INTPOL
  SUBROUTINE INTPOL(I1,I1R,CGCUM,D,Z)
  DIMENSION R(20),CGCUM(20)
  VAL = (CGCUM(I1) - CGCUM(I1R))/(R(I1) - R(I1R))
  DIFF = Z - CGCUM(I1)
  TEMP = VAL * R(I1)
  D = (DIFF + TEMP)/VAL
  RETURN
END

```

TABLE A2.1.4 LISTING OF PROGRAM GENPAR2.

Program GENPAR2
to generate hydraulic and transport parameters
for a sandstone with authigenic minerals in the pore space.

```

451 READ(5,100)TITLE
452 WRITE(6,100)TITLE
453
454 C Input mineralogy, bulk properties of sample
455 C and properties of individual minerals
456 C
457 READ(5,100)TMIN
458 READ(5,200)NMIN,BULK
459 READ(5,300)D, PORTOT, PORMM, PERM
460 READ(5,400)CLAY,GF
461 DO 10 I = 1, NPROP
462 READ(5,500) (PROP(I,J), J = 1, NMIN)
463 10 CONTINUE
464 DO 20 J = 1, NMIN
465 SM(J) = PROP(1,J)
466 RHO(J) = PROP(2,J)
467 CATEC(J) = PROP(3,J)
468 FRAC(J) = PROP(4,J)
469 20 CONTINUE
470 WRITE(6,201) CO
471 WRITE(6,1901)CLAY
472 IF(PORMM.NE.0.) WRITE(6,501) PORMM, PORTOT
473 WRITE(6,601)
474 WRITE(6,701) NMIN, TMIN
475 WRITE(6,801)
476 DO 30 J = 1, NMIN
477 WRITE(6,901) J, (PROP(I,J), I = 1, NPROP)
478 30 CONTINUE
479
480 C 2 Calculate permeability, dispersivity and CEC of sample
481 C
482 CALL PERM2(PORTOT, PORMM, F, CO, PERM, RHO, FRAC, SM, NMIN, CLAY, SS, GF)
483 IF(DL.EQ.0.)CALL DISPER(DZERO, F, PORTOT, PORMM, D, GAMMA, PERM
484 1, FMU, GRAD, DSP, DL, II, VMM, PE)
485 CALL CATPP(SM, NMIN, CATEC, PROD, BULK, PORTOT, SS, RHO, FRAC, CLAY)
486 WRITE(6,1201)
487
488 C Output results
489 C
490 WRITE(6,1801)BULK
491 WRITE(6,1301)SS
492 WRITE(6,301) F
493 WRITE(6,401) PERM
494 IF(II.NE.2)WRITE(6,1401) DSP, DL, VMM, GRAD, PE
495 IF(II.NE.2)RATIO = DL/DZERO
496 WRITE(6,1001)RATIO
497 WRITE(6,1501) CATEX
498 WRITE(6,1601)
499 DO 40 I = 1, NMIN
500 WRITE(6,1701) I, PROD(I)

```



```

501 40 CONTINUE
502 50 CONTINUE
503 100 FORMAT(20A4)
504 200 FORMAT(15,F10.3)
505 300 FORMAT(4F10.3)
506 400 FORMAT(2F10.3)
507 500 FORMAT(10F6.3)
508 600 FORMAT(15)
509 101 FORMAT(1H1)
510 201 FORMAT(//2X,'PORE SHAPE FACTOR =',F10.3)
511 301 FORMAT(1X,'FORMATION FACTOR',9X,F10.3)
512 401 FORMAT(1X,'12HPERMEABILITY',13X,E10.4,1X,6HSQ,CM.)
513 501 FORMAT(//2X,'MACROPOROSITY =',F10.3//2X,'POROSITY =',F10.3)
514 601 FORMAT(//12X,'PROPERTIES OF MINERALS IN THE SIMULATION...')
515 701 FORMAT(//2X,'MINERALS 1 TO',13X,'//2X,20A4)
516 801 FORMAT('MINERAL',3X,'SM',5X,'RHO',3X,'CATEC',2X,'FRAC')
517 901 FORMAT(2X,13,2X,4F7.3)
518 1001 FORMAT(1X,'DL/DZERO',17X,F10.3)
519 1201 FORMAT(//12X,'COMPUTED PROPERTIES OF SAMPLE...')
520 1301 FORMAT(1X,'1GHSPECIFIC SURFACE',9X,F10.3,1X,8HSQ,M./G.)
521 1401 FORMAT(1X,'DISPERSIVITY',13X,E10.4,1X,'CM.'/1X,'LONGITUDINAL DISPE'
522 'RSION'/5X,'COEFFICIENT',10X,E10.4,1X,'SQ.CM./SEC.'/1X,'(AT FLUID'
523 '2VELOCITY OF',E10.4,1X,'CM./SEC.'/1X,'FOR HEAD GRADIENT OF',F10.2'
524 '3/1X',AND PECLET NUMBER OF',F10.3,')')
525 1501 FORMAT(1X,'CATION EXCH. CAPACITY',4X,F10.3,2X,'MEQ/100G')
526 1601 FORMAT(//5X,'C.E.C.(MEQ/100G) DUE TO EACH EXCHANGER...//2X,'MINERAL'
527 '1',5X,'C.E.C.')
528 1701 FORMAT(2X,13,8X,F7.3)
529 1801 FORMAT(//1X,'BULK DENSITY',13X,F10.3,1X,'G./CM**3')
530 1901 FORMAT(//2X,'PERCENTAGE OF CLAY =',F10.3)
531 STOP
532 END
533
534 C Subroutine PERM2
535 C
536 C
537 SUBROUTINE PERM2(PORTOT, PORMM, F, CO, PERM, RHO, FRAC, SM, NMIN, CLAY, SS,
538 1GF)
539 DIMENSION RHO(10), FRAC(10), SM(10), SO(10), S(10)
540 IF(PORMM.EQ.0.) GO TO 11
541 X = ALOG10(PORMM)/ALOG10(PORTOT)
542 G = 2.2 - (.67 * X)
543 GO TO 12
544 11 G = 1.03
545 X = 1.73
546 12 F = G * (PORTOT **(-X)) + (1 - G)
547
548 C Calculate effective specific surface in cm.**2/cm.**3
549 C and cm**2/g
550 C

```

```

551 SUM = 0.0
552 DO 10 I = 1, NMIN
553 SM(I) = SM(I) * 1.0E4
554 SO(I) = FRAC(I) * RHO(I) * SM(I)
555 S(I) = SO(I)/RHO(I)
556 SUM = SUM + SO(I)
557 10 CONTINUE
558 CUMSS = 0.0
559 DO 20 I = 1, NMIN
560 CUMSS = CUMSS + S(I)
561 20 CONTINUE
562 SS = CUMSS
563 SS = SS/1.0E4
564 IF (CLAY.GT..15) GF = GF * .1
565
566 C Calculate permeability
567 C
568 IF (CLAY.EQ.0.) GO TO 21
569 SUM = SUM * GF * CLAY
570 21 EMM = PORTOT/(SUM * (1 - PORTOT))
571 PERM = ((EMM * EMM)/CO) * (F**(-1.5))
572 RETURN
573 END
574
575 C Subroutine DISPER
576 C
577 SUBROUTINE DISPER(DZERO,F,PORTOT,PORMM,D,GAMMA,PERM,FMU,
578 1GRAD,DSP,DL,I1,VMM,PE)
579 C
580 Calculate seepage velocity
581 C
582 TAU = PORTOT * F
583 VEL = (PERM/PORTOT * SORT(TAU)) * (GAMMA/FMU) * GRAD
584 IF (PORMM.NE.0.) VMM = VEL * (PORTOT/PORMM)
585 IF (PORMM.EQ.0.) VMM = VEL
586
587 C Calculate Peclet Number and D11/DO of sample
588 C
589 PE = (VMM * D)/DZERO
590 IF (PE.LT..01) GO TO 14
591 PERM = PERM * 1.01E10
592 IF (PERM.GT.2000.0R,PERM.LT..0010) GO TO 13
593 DSIGMA = -.0241 - (.00219 * SORT(PERM)) - (.1071 * PORTOT) + (.04345 * F)
594 IF (PE.GE.100.) GO TO 11
595 RATIO = (1./F * PORTOT) + 0.5 * ((VMM * DSIGMA)/DZERO) + 1.1
596 DL = RATIO * DZERO
597 GO TO 12
598 11 RATIO = (1./F * PORTOT) + 0.5 * ((VMM * DSIGMA)/DZERO)
599 DL = RATIO * DZERO
600 12 DSP = DL/VMM

```

```

601 PERM = PERM * 9.87E-11
602 RETURN
603
604 13 WRITE(6,101)
605
606 PERM = PERM * 9.87E-11
607
608 101 FORMAT(/1X,'PERMEABILITY VALUE OUT OF RANGE OF VALIDITY'/1X,
609 'FOR ESTIMATION OF DISPERSIVITY')
610 RETURN
611
612 14 DL = 0.67 * DZERO
613 DSP = DL/VMM
614 RETURN
615 END
616
617 C Subroutine CATPP
618 C
619 SUBROUTINE CATPP(SM,NMIN,CATEX,PROD,BULK,PORTOT,SS,
620 RHO,FRAC,CLAY)
621 DIMENSION SM(10), S(10), CATEX(10), RHO(10), PROD(10), FRAC(10)
622
623 C Calculate bulk density of sample
624
625 SUM = 0.
626 DO 10 I = 1, NMIN
627 PROD(I) = FRAC(I) * RHO(I)
628 SUM = SUM + PROD(I)
629
630 10 CONTINUE
631 RHOAV = SUM
632 IF(BULK.EQ.O.)BULK = RHOAV * (1. - PORTOT)
633 IF(CATEX.NE.O.)GO TO 11
634
635 C Calculate bulk CEC of entire sample from mineralogy
636 C or from specific surface
637
638 SS = SS * (1. - PORTOT)
639 IF(SS.GE.15.AND.SS.LE.145.)CATEX = 11.102 * CLAY + .04259 * SS -
640 1.1988
641 IF(CATEX.EQ.O.)CALL CAT(FRAC,NMIN,CATEX,CATEX)
642
643 C Calculate CEC due to each mineral
644
645 11 SUM = 0.
646 DO 30 I = 1, NMIN
647 PROD(I) = FRAC(I) * CATEX(I)
648 SUM = SUM + PROD(I)
649
650 30 CONTINUE
651 DO 40 I = 1, NMIN
652 PROD(I) = (CATEX * PROD(I))/SUM
653
654 40 CONTINUE
655 RETURN
656 END

```

```
651 C
652 C Subroutine CAT
653 C
654 SUBROUTINE CAT(FRAC,NMIN,CATEC,CATEX)
655 DIMENSION FRAC(10),CATEC(10),S(10)
656 SUM = 0.0
657 DO 10 I = 1, NMIN
658 S(I) = FRAC(I) * CATEC(I)
659 SUM = SUM + S(I)
660 10 CONTINUE
661 CATEX = SUM
662 RETURN
663 END
664
665 .....
```


Applications of GENPAR1 and GENPAR2

The applications of GENPAR1 and GENPAR2 to simulated and actual sands and sandstones is illustrated with data from the simulated sediments of Chapter 2, the Milk River Formation and the Muddy Sandstone. Tables A3.2.1, A3.2.2 and A3.2.3, respectively, summarize the grain size distributions, parameters and amounts of silt and clay of the simulated sands. Tables A3.2.4 and A3.2.5 give examples of the input and output of GENPAR1 for the case of a sample for which the the grain size distribution and mineralogy are known. The application of GENPAR2 to the simulation of the parameters of a sandstone is demonstrated for the case of the Muddy Sandstone. Table A3.2.6 lists the input, and Table A3.2.7 the output of this case.

TABLE A3.2.1. GRAIN SIZE DISTRIBUTIONS OF SIMULATED SEDIMENTS.

Grain Size (cm.)	Fractional Wt.	Size Fraction
.....		
RUN 1		
0.17800	0.96000	1
0.10490	0.03510	2
0.07420	0.00150	3
0.05240	0.00140	4
0.04030	0.00040	5
0.03390	0.00020	6
0.02200	0.00020	7
0.00900	0.00020	8
RUN 2A		
0.45830	0.00030	1
0.38340	0.00170	2
0.29580	0.01600	3
0.21040	0.13200	4
0.14870	0.37000	5
0.10490	0.25000	6
0.07420	0.15000	7

0.05240	0.06400	8
0.04030	0.01120	9
0.03390	0.00120	10
0.02290	0.00260	11
RUN 2B		
0.45830	0.00200	1
0.38340	0.00200	2
0.29580	0.01600	3
0.21040	0.13000	4
0.14870	0.37000	5
0.10490	0.25000	6
0.07420	0.15500	7
0.05240	0.05000	8
0.04030	0.01500	9
0.03390	0.00300	10
0.02200	0.00300	11
0.01100	0.00220	12
0.00450	0.00080	13
RUN 3A		
0.45830	0.00350	1
0.38340	0.00250	2
0.29580	0.01900	3
0.21040	0.12500	4
0.14870	0.37000	5
0.10490	0.25000	6
0.07420	0.15500	7
0.05240	0.04000	8
0.04030	0.01900	9
0.03390	0.00600	10
0.02200	0.00520	11
0.01100	0.00180	12
0.00090	0.00200	13
RUN 3B		
0.45830	0.07000	1
0.38340	0.08000	2
0.29580	0.08000	3
0.21040	0.16000	4
0.14870	0.13000	5
0.10490	0.12000	6
0.07420	0.11000	7
0.05240	0.13000	8
0.04030	0.01000	9
0.03390	0.03500	10
0.02200	0.05000	11
0.01100	0.02150	12
0.00450	0.00250	13
RUN 4		
0.05000	0.00030	1
0.03834	0.00170	2
0.02958	0.99350	3
0.02104	0.00150	4
0.01487	0.00120	5
0.01049	0.00020	6
0.00742	0.00020	7

0.00524	0.00020	8
0.00250	0.00020	9
RUN 5A		
0.18000	0.00100	1
0.04583	0.39900	2
0.03834	0.14000	3
0.02958	0.24000	4
0.02104	0.16000	5
0.01487	0.05300	6
0.01049	0.00540	7
0.00900	0.00060	8
RUN 5B		
0.38340	0.00010	1
0.29580	0.00030	2
0.21040	0.00110	3
0.14870	0.00600	4
0.10490	0.01850	5
0.07420	0.05400	6
0.05240	0.22000	7
0.04030	0.20000	8
0.03390	0.18000	9
0.02200	0.24000	10
0.01100	0.07540	11
0.00460	0.00360	12
RUN 5C		
0.60000	0.00010	1
0.45830	0.00005	2
0.38340	0.00020	3
0.29580	0.00030	4
0.21040	0.00170	5
0.14870	0.00400	6
0.10490	0.01400	7
0.07420	0.07000	8
0.05240	0.21000	9
0.04030	0.20000	10
0.03390	0.18000	11
0.02200	0.24000	12
0.01100	0.07300	13
0.00120	0.00600	14
RUN 6A		
0.50000	0.00010	1
0.45830	0.00020	2
0.38340	0.00180	3
0.29580	0.00600	4
0.21040	0.02200	5
0.14870	0.05000	6
0.10490	0.08000	7
0.07420	0.14000	8
0.05240	0.12000	9
0.04030	0.10000	10
0.03390	0.06000	11
0.02200	0.17000	12
0.01100	0.17000	13
0.00550	0.07500	14

0.00100	0.02400	15
RUN 6B		
0.38340	0.00020	1
0.29580	0.00180	2
0.21040	0.01800	3
0.14870	0.06000	4
0.10490	0.08000	5
0.07420	0.12000	6
0.05240	0.12000	7
0.04030	0.10000	8
0.03390	0.06000	9
0.02200	0.17000	10
0.01100	0.17000	11
0.00550	0.00200	12
0.00400	0.00700	13
RUN 7		
0.02104	0.00200	1
0.01487	0.00300	2
0.01049	0.04500	3
0.00742	0.93000	4
0.00524	0.00200	5
0.00403	0.00700	6
0.00339	0.00600	7
0.00220	0.00300	8
0.00105	0.00100	9
RUN 8A		
0.04000	0.00010	1
0.02958	0.01490	2
0.02104	0.00500	3
0.01487	0.08000	4
0.01049	0.24000	5
0.00742	0.34000	6
0.00524	0.25000	7
0.00403	0.05000	8
0.00339	0.01500	9
0.00220	0.00400	10
RUN 8B		
0.06000	0.00010	1
0.04583	0.00040	2
0.03834	0.00050	3
0.02958	0.00400	4
0.02104	0.02000	5
0.01487	0.08500	6
0.01049	0.24000	7
0.00742	0.33000	8
0.00524	0.25000	9
0.00403	0.05000	10
0.00339	0.01400	11
0.00220	0.00200	12
0.00110	0.00200	13
0.00060	0.00100	14
RUN 8C		
0.09000	0.00010	1
0.04583	0.00090	2

0.03834	0.00100	3
0.02958	0.00400	4
0.02104	0.02400	5
0.01487	0.08000	6
0.01049	0.24000	7
0.00742	0.34000	8
0.00524	0.25000	9
0.00403	0.04500	10
0.00339	0.01300	11
0.00220	0.00900	12
0.00110	0.00060	13
0.00055	0.00040	14
0.00018	0.00100	15
RUN 9A		
0.10000	0.00010	1
0.04583	0.02990	2
0.03834	0.02400	3
0.02958	0.04600	4
0.02104	0.20000	5
0.01487	0.12000	6
0.01049	0.11000	7
0.00742	0.13000	8
0.00524	0.14000	9
0.00403	0.07000	10
0.00339	0.05000	11
0.00220	0.09000	12
0.00110	0.06500	13
0.00055	0.02100	14
0.00020	0.00300	15
RUN 9B		
0.04583	0.00010	1
0.03834	0.00090	2
0.02958	0.04900	3
0.02104	0.12000	4
0.01487	0.15000	5
0.01049	0.11000	6
0.00742	0.13000	7
0.00524	0.14000	8
0.00403	0.07000	9
0.00339	0.05000	10
0.00220	0.09000	11
0.00110	0.07200	12
0.00055	0.01600	13
0.00045	0.00100	14
RUN 10		
0.00300	0.00010	1
0.00210	0.00020	2
0.00149	0.00970	3
0.00105	0.98500	4
0.00074	0.00120	5
0.00052	0.00130	6
0.00040	0.00060	7
0.00034	0.00020	8
0.00030	0.00070	9

RUN 11A

0.00458	0.00030	1
0.00383	0.00170	2
0.00296	0.02800	3
0.00210	0.19000	4
0.00149	0.32000	5
0.00105	0.24000	6
0.00074	0.16000	7
0.00052	0.04900	8
0.00040	0.00700	9
0.00034	0.00100	10
0.00023	0.00200	11

RUN 11B

0.00800	0.00010	1
0.00458	0.00390	2
0.00383	0.00800	3
0.00296	0.04800	4
0.00210	0.16000	5
0.00149	0.32000	6
0.00105	0.24000	7
0.00074	0.16000	8
0.00052	0.04600	9
0.00040	0.00900	10
0.00034	0.00080	11
0.00022	0.00220	12
0.00011	0.00060	13
0.00008	0.00040	14

RUN 11C

0.00458	0.01200	1
0.00383	0.00800	2
0.00296	0.05000	3
0.00210	0.15000	4
0.00149	0.32000	5
0.00105	0.24000	6
0.00074	0.16000	7
0.00052	0.04200	8
0.00040	0.01000	9
0.00034	0.00300	10
0.00022	0.00120	11
0.00011	0.00210	12
0.00001	0.00070	13

RUN 12A

0.00917	0.00600	1
0.00458	0.09400	2
0.00383	0.04000	3
0.00296	0.10000	4
0.00210	0.15500	5
0.00149	0.12500	6
0.00105	0.11000	7
0.00074	0.12000	8
0.00052	0.09000	9
0.00040	0.05000	10
0.00034	0.03500	11
0.00022	0.04500	12

0.00011	0.02400	13
0.00002	0.00500	14
RUN 12B		
0.00596	0.00700	1
0.00458	0.04800	2
0.00383	0.05500	3
0.00296	0.13000	4
0.00210	0.14000	5
0.00149	0.14000	6
0.00105	0.11000	7
0.00074	0.12000	8
0.00052	0.09000	9
0.00040	0.05000	10
0.00034	0.03500	11
0.00022	0.04500	12
0.00011	0.02460	13
0.00006	0.00440	14

TABLE A3.2.2. PARAMETERS OF THE GRAIN SIZE DISTRIBUTIONS.

Run	UC	d_{80}	d_{10}	d_{50}	RF	RFF
1	1	.15	.15	.15	0	19.78
2A	2	.16	.08	.15	0	20.13
2B	2	.16	.08	.15	0	101.84
2C	2	.16	.08	.15	.002	509.22
3A	5	.20	.04	.15	.006	509.17
3B	5	.20	.04	.15	0	101.84
4	1	.04	.04	.04	0	20.00
5A	2	.046	.023	.04	0	20.00
5B	2	.046	.023	.04	0	83.35
5C	2	.046	.023	.04	.006	500.00
6A	5	.055	.011	.04	.024	500.00
6B	5	.055	.011	.04	0	95.85
7	1	.009	.009	.009	.010	20.04
8A	2	.011	.006	.009	.019	18.18
8B	2	.011	.006	.009	.019	100.00
8C	2	.011	.006	.009	.024	500.00
9A	5	.012	.002	.009	.229	500.00
9B	5	.012	.002	.009	.229	101.84
10	1	.0015	.0015	.0015	.999	10.00
11A	2	.0017	.0008	.0015	.999	19.93
11B	2	.0017	.0008	.0015	.995	100.00
11C	2	.0017	.0008	.0015	.987	509.20
12A	5	.0020	.0004	.0015	.899	509.17
12B	5	.002	.0004	.0015	.944	99.30

TABLE A3.2.3. SILT AND CLAY SIZE COMPOSITION OF
SIMULATED SEDIMENTS.

Run	Silt	vf silt	clay
7	.018	0	0
8A	.319	0	0
8B	.318	.001	0
9B	.650	.001	0
10	.995	.003	0
11A	.780	.216	.003
11B	.760	.210	.020
11C	.780	.212	.007
12A	.623	.260	.109
12B	.630	.260	.109

TABLE A3.2.4. SAMPLE OF INPUT DATA TO GENPART.

2									
'TYPICAL' MILK RIVER SANDSTONE (MEYBOOM, 1960)									
SMECKAOLILLTCHLRFSPRMICAQRTZ									
SMECTITE, KAOLINITE, ILLITE, CHLORITE, FELDSPAR, MICA, QUARTZ									
8 7 1.0									
.0354	.0177	.0088	.00438	.00216	.00108	.00055	.00026		
.0096	.0144	.5000	.2500	.0433	.0913	.0673	.0240		
0.000		0.000		0.000		0.000		0.000	
0.000		0.000		0.000		0.000	1.5E-6	0.000	
25.	15.	17.	17.	10.	12.	7.			
2.64	2.63	2.80	2.80	2.60	2.85	2.65			
110.	12.	30.	30.	.15	1.80	1E-2			
.00	.00	.00	.00	.00	.00	.00	.28		
.00	.00	.00	.00	.00	.00	.00	.52		
.00	.00	.00	.00	.00	.00	.00	.17		
.00	.00	.00	.00	.00	.00	.00	.03		
.04	.04	.04	.04	.04	.04	.04	.00		
.03	.03	.03	.03	.03	.03	.03	.00		
.93	.93	.93	.93	.93	.93	.93	.00		
'TYPICAL' MILK RIVER SHALE (MEYBOOM, 1960)									
SMECKAOLILLTCHLRFSPRMICAQRTZ									
SMECTITE, KAOLINITE, ILLITE, CHLORITE, FELDSPAR, MICA, QUARTZ									
9 7 1.0									
.0354	.0177	.0088	.00438	.00216	.00108	.00055	.00026	.00013	
.0050	.0150	.4100	.1300	.1050	.08500	.0900	.1300	.0300	
0.000		0.000		0.000		0.000	0.000	0.000	
0.000		0.000		0.000		0.000	1.5E-6	0.000	
25.	15.	17.	17.	10.	12.	7.			
2.64	2.63	2.80	2.80	2.60	2.85	2.65			
110.	12.	30.	30.	.15	1.80	1E-2			
.00	.00	.00	.00	.00	.00	.00	.28	.28	
.00	.00	.00	.00	.00	.00	.00	.52	.52	
.00	.00	.00	.00	.00	.00	.00	.17	.17	
.00	.00	.00	.00	.00	.00	.00	.03	.03	
.04	.04	.04	.04	.04	.04	.04	.00	.00	
.03	.03	.03	.03	.03	.03	.03	.00	.00	
.93	.93	.93	.93	.93	.93	.93	.00	.00	

TABLE A3.2.5. SAMPLE OUTPUT FROM GENPARI.

'TYPICAL' MILK RIVER SANDSTONE (WEYBOOM, 1960)

GRAIN SIZE DISTRIBUTION...

GRAIN SIZE (CM.)	FRACTIONAL WT.	SIZE FRACTION
0.03540	0.00960	1
0.01770	0.01440	2
0.00880	0.50000	3
0.00438	0.25000	4
0.00216	0.04330	5
0.00108	0.09130	6
0.00055	0.06730	7
0.00026	0.02400	8

MINERALS IN THE SIMULATION...

SMECTITE, KAOLINITE, ILLITE, CHLORITE, FELDSPAR, MICA, QUARTZ

PROPERTIES OF MINERALS IN THE SIMULATION...

DENSITY	SMEC	KAOL	ILLT	CHLR	FSPR	MICA	QRTZ
SH. FACTOR	2.64	2.63	2.80	2.80	2.60	2.85	2.65
C.E.C.	110.000	15.00	17.00	17.00	10.00	12.00	7.00
		12.000	30.000	30.000	0.150	1.800	0.000

MINERAL CONC. IN EACH SIZE FRACTION...

1	2	3	4	5	6	7	8
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.28	0.52	0.17	0.03	0.04	0.04	0.03	0.93

FINES RATIO = 0.226

SIZE RATIO = 136.154

MOLEC. DIFFUSION COEFF. = 0.150000E-05

'TYPICAL' MILK RIVER SANDSTONE (MEYBOOM, 1960)

PERM. SHAPE COEFF., SAND = 7.270

PERM. SHAPE COEFF., SILT = 7.270

PERM. SHAPE COEFF., CLAY = 18.200

COMPUTED PROPERTIES OF SAMPLE...

BULK DENSITY 1.825 G./CM.³
 POROSITY 0.312
 UNIFORMITY COEFFICIENT 9.31
 D₁₀ 0.00118 CM.
 D₅₀ 0.00923 CM.
 D₆₀ 0.01101 CM.
 SPECIFIC SURFACE 0.4166E+04 /CM.
 PERMEABILITY 0.7434E-09 SQ. CM.
 DISPERSIVITY 0.3013E-02 CM.
 LONGITUDINAL DISPERSION
 COEFFICIENT 0.7667E-04 SQ. CM./SEC.
 (*AT FLUID VELOCITY OF 0.2545E-01 CM./SEC.
 FOR HEAD GRADIENT OF 100.00
 AND PECLET NO. OF 156.527)
 DL/DZERO 51.111
 CATION EXCH. CAPACITY 1.092 MEQ/100G

C.E.C. (MEQ/100G) DUE TO EACH EXCHANGER...
 SMEC KAOL ILLT CHLR FSPR
 0.739 0.150 0.122 0.022 0.006
 'TYPICAL' MILK RIVER SHALE (MEYBOOM, 1960)

MICA 0.053
 QRTZ 0.000

GRAIN SIZE DISTRIBUTION...

GRAIN SIZE (CM.)	FRACTIONAL WT.	SIZE FRACTION
0.03540	0.00500	1
0.01770	0.01500	2
0.00880	0.41000	3
0.00438	0.13000	4
0.00216	0.10500	5
0.00108	0.08500	6

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99
100

0.00055 0.09000 7
0.00026 0.13000 8
0.00013 0.03000 9

MINERALS IN THE SIMULATION...

SMECTITE, KAOLINITE, ILLITE, CHLORITE, FELDSPAR, MICA, QUARTZ

PROPERTIES OF MINERALS IN THE SIMULATION...

DENSITY	SH. FACTOR	C.E.C.	SMEC	KAOL	ILLY	CHLR	FSPR	MICA	QRTZ
2.64	25.00	110.000	2.63	2.80	2.80	2.60	2.85	2.65	2.65
15.00	15.00	17.00	17.00	17.00	17.00	10.00	12.00	7.00	7.00
30.000	30.000	30.000	30.000	30.000	30.000	0.150	1.800	0.000	0.000

MINERAL CONC. IN EACH SIZE FRACTION...

1	2	3	4	5	6	7	8	9
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.28	0.28	0.52	0.17	0.03	0.03	0.0	0.0	0.0
0.28	0.28	0.52	0.17	0.03	0.03	0.0	0.0	0.0

FINES RATIO = 0.440

SIZE RATIO = 272.308

MOLEC. DIFFUSION COEFF. = 0.150000E-05

'TYPICAL' MILK RIVER SHALE (MEYBOOM, 1960)

PERM. SHAPE COEFF., SAND = 7.270

PERM. SHAPE COEFF., SILT = 7.270

PERM. SHAPE COEFF., CLAY = 18.200

COMPUTED PROPERTIES OF SAMPLE...

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151	BULK DENSITY	2.040	G./CM. ⁺⁺³
152	POROSITY	0.232	
153	UNIFORMITY COEFFICIENT	22.71	
154	D10	0.00042 CM.	
155	D50	0.00642 CM.	
156	D60	0.00845 CM.	
157	SPECIFIC SURFACE	0.1598E+05 /CM.	
158	PERMEABILITY	0.1653E-10 SQ.CM.	
159	DISPERSIVITY	0.4010E-02 CM.	
160	LONGITUDINAL DISPERSION		
161	COEFFICIENT	0.3678E-05 SQ.CM./SEC*	
162	(*AT FLUID VELOCITY OF	0.8640E-03 CM./SEC.	
163	FOR HEAD GRADIENT OF	100.00	
164	AND PECLET NO. OF	3.698)	
165	DL/DZERO	2.452	
166	CATION EXCH. CAPACITY	6.937	MEQ/100G
167			
168	C.E.C. (MEQ/100G) DUE TO EACH EXCHANGER...		
169	SMEC	4.928	
170	KADL	0.998	
171	ILLT	0.816	
	CHLR	0.144	
	FSPR	0.005	
	MICA	0.045	
	ORTZ	0.000	

TABLE A3.2.6. SAMPLE OF INPUT TO GENPAR2.

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10
MUDDY SANDSTONE, RUN B (DIAG. ZONE B, SED. ZONE 4): LAYER 1
QRTZ(D),FSPAR,MICA,RK FRAGS,QRTZ(A),ILLT,CHLOR,KAOL,MONT
  9      .000
      .018      .220      .000      .000
      .350      .011
1.5E-61.0E-3 0.1001.0E-4 .002 110. 42. 27. 82.
2.650 2.600 2.850 2.950 2.650 2.850 2.950 2.630 2.600
.001 .05 1.80 .005 .00125.00030.000 9.00090.000
.580 .009 .052 .009 .228 .012 .017 .070 .023
MUDDY SANDSTONE, RUN B, LAYER 2
QRTZ(D),FSPAR,MICA,RK FRAGS,QRTZ(A),ILLT,CHLOR,KAOL,MONT
  9      .000
      .015      .170      .000      .000
      .330      .011
1.5E-61.0E-3 0.1001.0E-4 .002 110. 42. 27. 82.
2.650 2.600 2.850 2.950 2.650 2.850 2.950 2.630 2.600
.001 .05 1.80 .005 .00125.00030.000 9.00090.000
.650 .003 .014 .003 .214 .011 .016 .067 .022
MUDDY SANDSTONE, RUN B, LAYER 3
QRTZ(D),FSPAR,MICA,RK FRAGS,QRTZ(A),ILLT,CHLOR,KAOL,MONT
  9      .000
      .016      .180      .000      .000
      .080      .020
1.5E-61.0E-3 0.1001.0E-4 .002 110. 42. 27. 82.
2.650 2.600 2.850 2.950 2.650 2.850 2.950 2.630 2.600
.001 .05 1.80 .005 .00125.00030.000 9.00090.000
.870 .007 .036 .007 .052 .003 .004 .016 .005
MUDDY SANDSTONE, RUN B, LAYER 4
QRTZ(D),FSPAR,MICA,RK FRAGS,QRTZ(A),ILLT,CHLOR,KAOL,MONT
  9      .000
      .015      .170      .000      .000
      .290      .011
1.5E-61.0E-3 0.1001.0E-4 .002 110. 42. 27. 82.
2.650 2.600 2.850 2.950 2.650 2.850 2.950 2.630 2.600
.001 .05 1.80 .005 .00125.00030.000 9.00090.000
.620 .012 .066 .012 .189 .009 .014 .058 .020
MUDDY SANDSTONE, RUN B, LAYER 5
QRTZ(D),FSPAR,MICA,RK FRAGS,QRTZ(A),ILLT,CHLOR,KAOL,MONT
  9      .000
      .010      .100      .000      .000
      .310      .042
1.5E-51.0E-3 0.1001.0E-4 .002 110. 42. 27. 82.
2.650 2.600 2.850 2.950 2.650 2.850 2.950 2.630 2.600
.001 .05 1.80 .005 .00125.00030.000 9.00090.000
.670 .003 .014 .003 .202 .010 .015 .062 .021
MUDDY SANDSTONE, RUN B, LAYER 6
QRTZ(DETRITAL),FELDSPAR,MICA,ROCK FRAGMENTS
  4      .000
      .018      .220      .000      .000
      .000      .011
1.5E-61.0E-3 0.1001.0E-4

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2.650 2.600 2.850 2.950
 .001 .05 1.80 .005
 .950 .007 .036 .007

MUDDY SANDSTONE, RUN B, LAYER 7

QRTZ(D), FSPAR, MICA, RK FRAGS, QRTZ(A), ILLT, CHLOR, KAOL, MONT
 9 .000

.015 .170 .000 .000
 .250 .016

1.5E-5 1.0E-3 0.100 1.0E-4 .002 110. 42. 27. 82.
 2.650 2.600 2.850 2.950 2.650 2.850 2.950 2.630 2.600
 .001 .05 1.80 .005 .00125.00030.000 9.00090.000
 .550 .030 .140 .030 .162 .008 .012 .050 .018

MUDDY SANDSTONE, RUN B, LAYER 8

QUARTZ(D), QUARTZ(A), ILLITE, CHLORITE, KAOLINITE, MONTMORILLONITE

6 .000

.015 .170 .000 .000
 .100 .011

1.5E-5 .002 110. 42. 27. 82.
 2.650 2.650 2.850 2.950 2.630 2.600
 .001 .00125.00030.000 9.00090.000
 .900 .064 .004 .006 .020 .006

MUDDY SANDSTONE, RUN B, LAYER 9

QUARTZ(D), QUARTZ(A), ILLITE, CHLORITE, KAOLINITE, MONTMORILLONITE

6 .000

.014 .160 .000 .000
 .050 .083

1.5E-5 .002 110. 42. 27. 82.
 2.650 2.650 2.850 2.950 2.630 2.600
 .001 .00125.00030.000 9.00090.000
 .950 .032 .002 .003 .010 .003

MUDDY SANDSTONE, RUN B, LAYER 10

QUARTZ(D), QUARTZ(A), ILLITE, CHLORITE, KAOLINITE, MONTMORILLONITE

6 .000

.018 .220 .000 .000
 .020 .160

1.5E-5 .002 110. 42. 27. 82.
 2.650 2.650 2.850 2.950 2.630 2.600
 .001 .00125.00030.000 9.00090.000
 .980 .013 .001 .001 .004 .001

TABLE A3.2.7. SAMPLE OF OUTPUT FROM GENPAR2.

1
MUDDY SANDSTONE, RUN B (DIAG. ZONE B, SED. ZONE 4): LAYER 1

PORE SHAPE FACTOR = 2.500

PERCENTAGE OF CLAY = 0.350

PROPERTIES OF MINERALS IN THE SIMULATION...

MINERALS 1 TO 9:
QRTZ(D), FSPAR, MICA, RK FRAGS, QRTZ(A), ILLT, CHLOR, KAOL, MONT

MINERAL	SM	RHO	CATEC	FRAC
1	0.000	2.650	0.001	0.580
2	0.001	2.600	0.050	0.009
3	0.100	2.850	1.800	0.052
4	0.000	2.950	0.005	0.009
5	0.002	2.650	0.001	0.228
6	110.000	2.850	25.000	0.012
7	42.000	2.950	30.000	0.017
8	27.000	2.630	9.000	0.070
9	82.000	2.600	90.000	0.023

COMPUTED PROPERTIES OF SAMPLE...

BULK DENSITY	2.081 G./CM**3
SPECIFIC SURFACE	4.536 SQ.M./G.
FORMATION FACTOR	14.110
PERMEABILITY	0.1626E-06 SQ.CM.
DISPERSIVITY	0.2383E+00 CM.
LONGITUDINAL DISPERSION	
COEFFICIENT	0.2716E-01 SQ.CM./SEC*
(*AT FLUID VELOCITY OF 0.1140E+00 CM./SEC.	
FOR HEAD GRADIENT OF	1.00
AND PECLET NUMBER OF	1368.064)
DL/DZERO	18108.785
CATION EXCH. CAPACITY	3.605 MEQ/100G

C.E.C.(MEQ/100G) DUE TO EACH EXCHANGER...

MINERAL	C.E.C.
1	0.001
2	0.000
3	0.094
4	0.000
5	0.000
6	0.300
7	0.510
8	0.630
9	2.070

1
MUDDY SANDSTONE, RUN B, LAYER 2

PORE SHAPE FACTOR = 2.500

PERCENTAGE OF CLAY = 0.330

PROPERTIES OF MINERALS IN THE SIMULATION...

MINERALS 1 TO 9:
QRTZ(D), FSPAR, MICA, RK FRAGS, QRTZ(A), ILLT, CHLOR, KAOL, MONT

MINERAL	SM	RHO	CATEC	FRAC
1	0.000	2.650	0.001	0.650
2	0.001	2.600	0.050	0.003
3	0.100	2.850	1.800	0.014
4	0.000	2.950	0.005	0.003
5	0.002	2.650	0.001	0.214
6	110.000	2.850	25.000	0.011
7	42.000	2.950	30.000	0.016
8	27.000	2.630	9.000	0.067
9	82.000	2.600	90.000	0.022

COMPUTED PROPERTIES OF SAMPLE...

BULK DENSITY	2.206 G./CM**3
SPECIFIC SURFACE	4.562 SQ.M./G.
FORMATION FACTOR	22.058
PERMEABILITY	0.5531E-07 SQ.CM.
DISPERSIVITY	0.4321E+00 CM.
LONGITUDINAL DISPERSION	
COEFFICIENT	0.2384E-01 SQ.CM./SEC*
(*AT FLUID VELOCITY OF	0.5516E-01 CM./SEC.
FOR HEAD GRADIENT OF	1.00
AND PECLET NUMBER OF	551.637)
DL/DZERO	15892.199
CATION EXCH. CAPACITY	3.364 MEQ/100G

C.E.C. (MEQ/100G) DUE TO EACH EXCHANGER...

MINERAL	C.E.C.
1	0.001
2	0.000
3	0.025
4	0.000
5	0.000
6	0.275
7	0.480
8	0.603
9	1.980

1
MUDDY SANDSTONE, RUN B, LAYER 3

PORE SHAPE FACTOR = 2.500
 PERCENTAGE OF CLAY = 0.080

PROPERTIES OF MINERALS IN THE SIMULATION...

MINERALS 1 TO 9:
 QRTZ(D), FSPAR, MICA, RK FRAGS, QRTZ(A), ILLT, CHLOR, KAOL, MONT

MINERAL	SM	RHO	CATEC	FRAC
1	0.000	2.650	0.001	0.870
2	0.001	2.600	0.050	0.007
3	0.100	2.850	1.800	0.036
4	0.000	2.950	0.005	0.007
5	0.002	2.650	0.001	0.052
6	110.000	2.850	25.000	0.003
7	42.000	2.950	30.000	0.004
8	27.000	2.630	9.000	0.016
9	82.000	2.600	90.000	0.005

COMPUTED PROPERTIES OF SAMPLE...

BULK DENSITY	2.181 G./CM**3
SPECIFIC SURFACE	1.102 SQ.M./G.
FORMATION FACTOR	19.979
PERMEABILITY	0.6313E-07 SQ.CM.
DISPERSIVITY	0.3847E+00 CM.
LONGITUDINAL DISPERSION	
COEFFICIENT	0.2240E-01 SQ.CM./SEC*
(*AT FLUID VELOCITY OF	0.5823E-01 CM./SEC.
FOR HEAD GRADIENT OF	1.00
AND PECLET NUMBER OF	621.106)
DL/DZERO	14931.824
CATION EXCH. CAPACITY	0.855 MEQ/100G

C.E.C. (MEQ/100G) DUE TO EACH EXCHANGER...

MINERAL	C.E.C.
1	0.001
2	0.000
3	0.065
4	0.000
5	0.000
6	0.075
7	0.120
8	0.144
9	0.450

1
 MUDDY SANDSTONE, RUN B, LAYER 4

PORE SHAPE FACTOR = 2.500

PERCENTAGE OF CLAY = 0.290

PROPERTIES OF MINERALS IN THE SIMULATION...

MINERALS 1 TO 9:
QRTZ(D), FSPAR, MICA, RK FRAGS, QRTZ(A), ILLT, CHLOR, KAOL, MONT

MINERAL	SM	RHO	CATEC	FRAC
1	0.000	2.650	0.001	0.620
2	0.001	2.600	0.050	0.012
3	0.100	2.850	1.800	0.066
4	0.000	2.950	0.005	0.012
5	0.002	2.650	0.001	0.189
6	110.000	2.850	25.000	0.009
7	42.000	2.950	30.000	0.014
8	27.000	2.630	9.000	0.058
9	82.000	2.600	90.000	0.020

COMPUTED PROPERTIES OF SAMPLE...

BULK DENSITY 2.216 G./CM**3
 SPECIFIC SURFACE 3.977 SQ.M./G.
 FORMATION FACTOR 22.058
 PERMEABILITY 0.9449E-07 SQ.CM.
 DISPERSIVITY 0.4242E+00 CM.
 LONGITUDINAL DISPERSION
 COEFFICIENT 0.3997E-01 SQ.CM./SEC*
 (*AT FLUID VELOCITY OF 0.9424E-01 CM./SEC.
 FOR HEAD GRADIENT OF 1.00
 AND PECLET NUMBER OF 942.364)
 DL/DZERO 26648.707
 CATION EXCH. CAPACITY 3.087 MEQ/100G

C.E.C. (MEQ/100G) DUE TO EACH EXCHANGER...

MINERAL	C.E.C.
1	0.001
2	0.001
3	0.119
4	0.000
5	0.000
6	0.225
7	0.420
8	0.522
9	1.800

1
MUDDY SANDSTONE, RUN B, LAYER 5

PORE SHAPE FACTOR = 2.500

PERCENTAGE OF CLAY = 0.310

PROPERTIES OF MINERALS IN THE SIMULATION...

MINERALS 1 TO 9:
QRTZ(D), FSPAR, MICA, RK FRAGS, QRTZ(A), ILLT, CHLOR, KAOL, MONT

MINERAL	SM	RHO	CATEC	FRAC
1	0.000	2.650	0.001	0.670
2	0.001	2.600	0.050	0.003
3	0.100	2.850	1.800	0.014
4	0.000	2.950	0.005	0.003
5	0.002	2.650	0.001	0.202
6	110.000	2.850	25.000	0.010
7	42.000	2.950	30.000	0.015
8	27.000	2.630	9.000	0.062
9	82.000	2.600	90.000	0.021

COMPUTED PROPERTIES OF SAMPLE...

BULK DENSITY	2.392 G./CM**3
SPECIFIC SURFACE	4.615 SQ.M./G.
FORMATION FACTOR	55.284
PERMEABILITY	0.3668E-09 SQ.CM.
DISPERSIVITY	0.2399E+01 CM.
LONGITUDINAL DISPERSION	
COEFFICIENT	0.1811E-02 SQ.CM./SEC*
(*AT FLUID VELOCITY OF 0.7551E-03 CM./SEC.	
FOR HEAD GRADIENT OF	1.00
AND PECLET NUMBER OF	5.034)
DL/DZERO	1207.437
CATION EXCH. CAPACITY	3.174 MEQ/100G

C.E.C.(MEQ/100G) DUE TO EACH EXCHANGER...

MINERAL	C.E.C.
1	0.001
2	0.000
3	0.025
4	0.000
5	0.000
6	0.250
7	0.450
8	0.558
9	1.890

1
MUDDY SANDSTONE, RUN B, LAYER 6

PORE SHAPE FACTOR = 2.500

PERCENTAGE OF CLAY = 0.0

PROPERTIES OF MINERALS IN THE SIMULATION...

MINERALS 1 TO 4:
QRTZ(DETRITAL),FELDSPAR,MICA,ROCK FRAGMENTS

MINERAL	SM	RHO	CATEC	FRAC
1	0.000	2.650	0.001	0.950
2	0.001	2.600	0.050	0.007
3	0.100	2.850	1.800	0.036
4	0.000	2.950	0.005	0.007

COMPUTED PROPERTIES OF SAMPLE...

BULK DENSITY	2.074 G./CM**3
SPECIFIC SURFACE	0.003 SQ.M./G.
FORMATION FACTOR	14.110
PERMEABILITY	0.5659E-07 SQ.CM.
DISPERSIVITY	0.2565E+00 CM.
LONGITUDINAL DISPERSION	
COEFFICIENT	0.1018E-01 SQ.CM./SEC*
(*AT FLUID VELOCITY OF	0.3968E-01 CM./SEC.
FOR HEAD GRADIENT OF	1.00
AND PECLET NUMBER OF	476.144)
DL/DZERO	6784.699
CATION EXCH. CAPACITY	0.066 MEQ/100G

C.E.C.(MEQ/100G) DUE TO EACH EXCHANGER...

MINERAL	C.E.C.
1	0.001
2	0.000
3	0.065
4	0.000

1 MUDDY SANDSTONE, RUN B, LAYER 7

PORE SHAPE FACTOR = 2.500

PERCENTAGE OF CLAY = 0.250

PROPERTIES OF MINERALS IN THE SIMULATION...

MINERALS 1 TO 9:
QRTZ(D),FSPAR,MICA,RK FRAGS,QRTZ(A),ILLT,CHLOR,KAOL,MONT

MINERAL	SM	RHO	CATEC	FRAC
1	0.000	2.650	0.001	0.550
2	0.001	2.600	0.050	0.030
3	0.100	2.850	1.800	0.140
4	0.000	2.950	0.005	0.030
5	0.002	2.650	0.001	0.162
6	110.000	2.850	25.000	0.008

7	42.000	2.950	30.000	0.012
8	27.000	2.630	9.000	0.050
9	82.000	2.600	90.000	0.018

COMPUTED PROPERTIES OF SAMPLE...

BULK DENSITY	2.232 G./CM**3
SPECIFIC SURFACE	3.506 SQ.M./G.
FORMATION FACTOR	22.058
PERMEABILITY	0.7733E-07 SQ.CM.
DISPERSIVITY	0.4274E+00 CM.
LONGITUDINAL DISPERSION	
COEFFICIENT	0.3296E-01 SQ.CM./SEC*
(*AT FLUID VELOCITY OF	0.7712E-01 CM./SEC.
FOR HEAD GRADIENT OF	1.00
AND PECLET NUMBER OF	771.211)
DL/DZERO	21974.844
CATION EXCH. CAPACITY	2.884 MEQ/100G

C.E.C.(MEQ/100G) DUE TO EACH EXCHANGER...

MINERAL	C.E.C.
1	0.001
2	0.001
3	0.252
4	0.000
5	0.000
6	0.200
7	0.360
8	0.450
9	1.620

1
MUDDY SANDSTONE, RUN B, LAYER 8

PORE SHAPE FACTOR = 2.500

PERCENTAGE OF CLAY = 0.100

PROPERTIES OF MINERALS IN THE SIMULATION...

MINERALS 1 TO 6:

QUARTZ(D), QUARTZ(A), ILLITE, CHLORITE, KAOLINITE, MONTMORILLONITE

MINERAL	SM	RHO	CATEC	FRAC
1	0.000	2.650	0.001	0.900
2	0.002	2.650	0.001	0.064
3	110.000	2.850	25.000	0.004
4	42.000	2.950	30.000	0.006
5	27.000	2.630	9.000	0.020
6	82.000	2.600	90.000	0.006

COMPUTED PROPERTIES OF SAMPLE...

BULK DENSITY	2.201 G./CM**3
SPECIFIC SURFACE	1.431 SQ.M./G.
FORMATION FACTOR	22.058
PERMEABILITY	0.6048E-07 SQ.CM.
DISPERSIVITY	0.4310E+00 CM.
LONGITUDINAL DISPERSION	
COEFFICIENT	0.2599E-01 SQ.CM./SEC*
(*AT FLUID VELOCITY OF	0.6032E-01 CM./SEC.
FOR HEAD GRADIENT OF	1.00
AND PECLET NUMBER OF	603.188)
DL/DZERO	17329.707
CATION EXCH. CAPACITY	1.001 MEQ/100G

C.E.C.(MEQ/100G) DUE TO EACH EXCHANGER...

MINERAL	C.E.C.
1	0.001
2	0.000
3	0.100
4	0.180
5	0.180
6	0.540

1
MUDDY SANDSTONE, RUN B, LAYER 9

PORE SHAPE FACTOR = 2.500

PERCENTAGE OF CLAY = 0.050

PROPERTIES OF MINERALS IN THE SIMULATION...

MINERALS 1 TO 6:

QUARTZ(D), QUARTZ(A), ILLITE, CHLORITE, KAOLINITE, MONTMORILLONITE

MINERAL	SM	RHO	CATEC	FRAC
1	0.000	2.650	0.001	0.950
2	0.002	2.650	0.001	0.032
3	110.000	2.850	25.000	0.002
4	42.000	2.950	30.000	0.003
5	27.000	2.630	9.000	0.010
6	82.000	2.600	90.000	0.003

COMPUTED PROPERTIES OF SAMPLE...

BULK DENSITY

2.227 G./CM**3

SPECIFIC SURFACE 0.724 SQ.M./G.
 FORMATION FACTOR 24.501
 PERMEABILITY 0.1256E-07 SQ.CM.
 DISPERSIVITY 0.4993E+00 CM.
 LONGITUDINAL DISPERSION
 COEFFICIENT 0.6793E-02 SQ.CM./SEC*
 (*AT FLUID VELOCITY OF 0.1360E-01 CM./SEC.
 FOR HEAD GRADIENT OF 1.00
 AND PECLET NUMBER OF 126.978)
 DL/DZERO 4528.629
 CATION EXCH. CAPACITY 0.501 MEQ/100G

C.E.C.(MEQ/100G) DUE TO EACH EXCHANGER...

MINERAL	C.E.C.
1	0.001
2	0.000
3	0.050
4	0.090
5	0.090
6	0.270

1 MUDDY SANDSTONE, RUN B, LAYER 10

PORE SHAPE FACTOR = 2.500

PERCENTAGE OF CLAY = 0.020

PROPERTIES OF MINERALS IN THE SIMULATION...

MINERALS 1 TO 6:

QUARTZ(D), QUARTZ(A), ILLITE, CHLORITE, KAOLINITE, MONTMORILLONITE

MINERAL	SM	RHO	CATEC	FRAC
1	0.000	2.650	0.001	0.980
2	0.002	2.650	0.001	0.013
3	110.000	2.850	25.000	0.001
4	42.000	2.950	30.000	0.001
5	27.000	2.630	9.000	0.004
6	82.000	2.600	90.000	0.001

PERMEABILITY VALUE OUT OF RANGE OF VALIDITY
FOR ESTIMATION OF DISPERSIVITY

COMPUTED PROPERTIES OF SAMPLE...

BULK DENSITY 2.067 G./CM**3
 SPECIFIC SURFACE 0.267 SQ.M./G.
 FORMATION FACTOR 14.110
 PERMEABILITY 0.6689E-06 SQ.CM.

DL/DZERO 4528.629
CATION EXCH. CAPACITY 0.182 MEQ/100G

C.E.C. (MEQ/100G) DUE TO EACH EXCHANGER...

MINERAL	C.E.C.
1	0.001
2	0.000
3	0.025
4	0.030
5	0.036
6	0.090

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APPENDIX 4. CODE LISTINGS AND APPLICATIONS OF MOC

Definition of Variables, Listings and Flowcharts

The logic and operation of MOC and Subroutine CATEx have been described previously in Chapter 3. The main variables for these programs are defined in Table A4.1.1 and the schematic flow charts are drawn in Figures A4.1.1 and A4.1.2. An example of the input to MOC is given in Table A4.1.2, and the accompanying output is displayed in Table A4.1.3. The complete listing of MOC is provided in Table A4.1.4.

TABLE A4.1.1. DEFINITION OF VARIABLES, MOC.
Variable Definition

ALPHA	Parameter relating concentration and density (usually = 1)
BULKI(I)	Initial bulk density
CAVG(I,J)	Average concentration in cell defined by row i and column j of grid
CBAK(I)	Initial concentration of ion i on exchanger
CECI(I)	CEC of cell defined by row i and column j of grid
CHG(I)	Charge on ion i
CIMMOL(I)	Initial concentration of ion i in fluid
CON(I,J)	Concentration of ion j on particle i
CONC(I,J,K)	Concentration of ion k in cell defined by row i and column j of grid
COUNT(I,J)	Number of particles in cell defined by row i and column j of grid
DAVG	Mass concentration of tracer (currently set to zero within flow domain)
DELT	Time increment
DELX	Increment in X space direction
DELZ	Increment in Z space direction
DIL(I)	Longitudinal dispersivity of each layer
DIT(I)	Transverse dispersivity of each layer
ICOH(I,J)	ID values to yield spatial variability map

IEX(I)	Name(s) of exchanger(s)
ION(I)	Number of ions
ID	Identification of each layer ($1 \leq I \leq \text{NUNIT}$)
IOP	Name of ion
IPX(I)	Initial X coordinate of particle
IPZ(I)	Initial Z coordinate of particle
IT	Number of iterations per time step
KTOTAL	Total number of time steps
ME, MEM	Counters controlling the number of printouts of results
MF	Dummy for "remembering" the position of each particle
NC	Number of columns
NEQIL	Number of equilibrium ion exchange relations
NEX	Number of exchangers
NION	Number of cations
NLB	Column position of left boundary of contaminant
NOUP(J)	Column position of top boundary of sustem
NP	Particle counter
NPER	Number of particles added per time step
NR	Number of rows
NRB	Column position of right boundary of contaminant
NUNIT	Number of layers with different properties
RHO(I)	Initial density of fluid
PORI(I)	Initial porosity of layer
RHOI(I)	Initial density of fluid in layer i
SEL(I,J)	Selectivity coefficient of exchanger i for equilibrium relation j
TOL	Tolerance for convergence of exchange iterations
VIX(I)	Velocity in X direction within each layer
VIZ(I)	Velocity in Z direction within each layer
XIMEQ(I,J,K)	Initial concentration in layer i and exchanger j of ion k
XMEQ(I,J,K,L)	Concentration in cells i,j of ion l on exchanger k
XPOS(I)	Position of particle X
ZPOS(I)	Position of particle Z

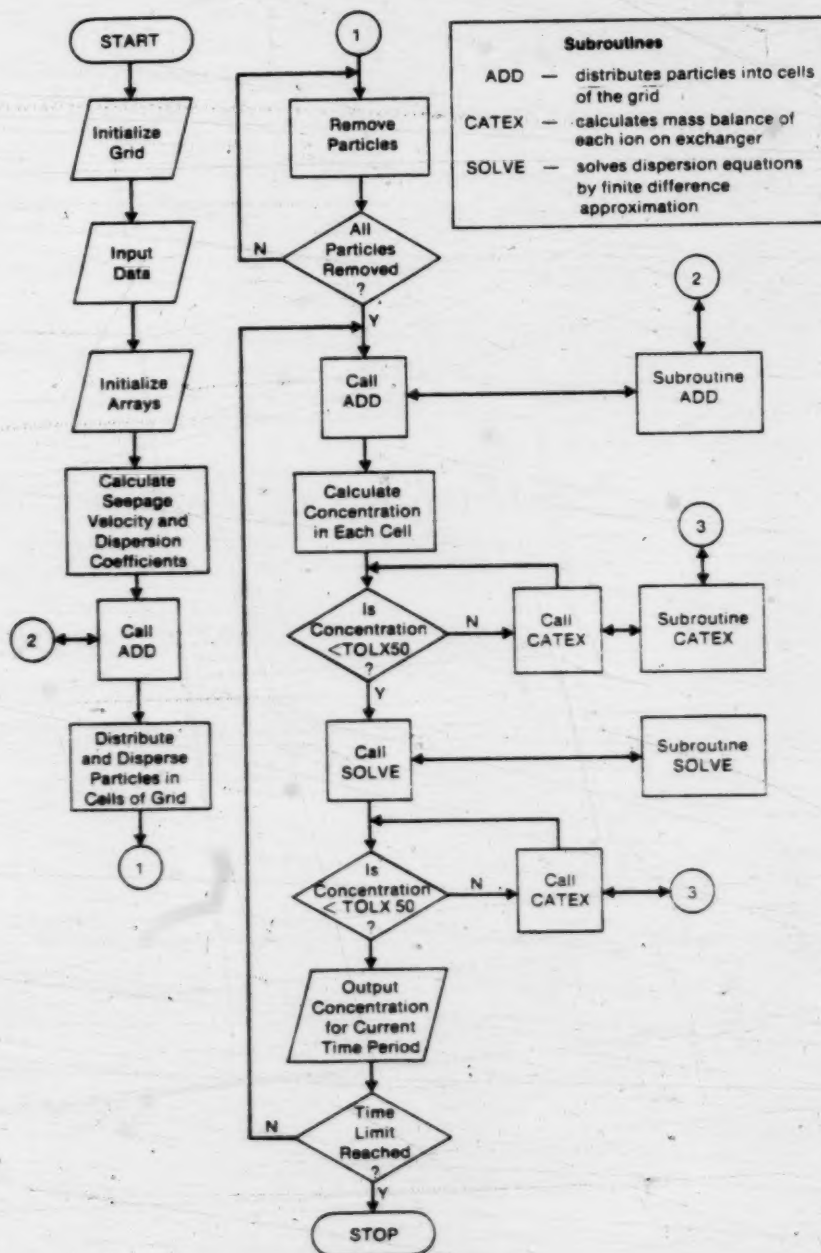


Figure A4.1.1. Simplified Flow Chart of MOC

TABLE A4.1.4. LISTING OF PROGRAM MOC.

```

C
C      Program MOC
C      to solve the advection-dispersion equation for
C      steady state mass transport in one- and two-
C      dimensions by the method of characteristics.
C      The solution is available for conservative
C      tracers and for the case of ion exchange adsorption.
C
C      Layout of Data File...
C      Line 1: TITLE (20A4)
C      Line 2: NR, NC, NPER, NLB, NRB, KTOTAL, MEM (7I5)
C      Line 3: NOUP(J), J=1, NC (24I3)
C      Line 4: DELX, DELZ, DELT, ALPHA, DAVG (5F10.2)
C      Line 5: NEX, NUNIT, NION, NEQIL, TOL (4I5, 1E10.3)
C      Line 6: ID, BULK(K), PORI(K), DIL(K), DIT(K), VIZ(K),
C      VIX(K), CEC(K, KK), K=1, NUNIT, KK=1, NEX (15, 9F10.3)
C      Line 7: IOP, ID, XIMEQ(K1, K2, K3), K1=1, NUNIT, K2=1, NEX,
C      K3=1, NION (1A5, 15, 10F5.2)
C      Line 8 et seq. : ICOH (80I1)
C      Line 9 et seq. : ION(I), CHG(I), CIMMOL(I), CRAK(I),
C      I=1, NION (1A5, 5F10.3)
C      Line 10 et seq. : IEX(I), SEL(I, J), I=1, NION, J=1, NEQIL
C      (1A5, 5F10.3)
C      Line 11: IPX, IPZ (2I5) (Optional)
C
C      COMMON ALPHA, DAVG, DELX, DELZ, DELT,
C      NCA, NP, NPER, IT, NLB, NRB, NEX, NION, NEQIL
C      DIMENSION RHO(40, 30), POR(40, 30), CAVG(40, 30), DELC(40, 30), D11(40, 30)
C      * DELB(40, 30, 3), DISPT(40, 30), SUMC(40, 30, 3), BULK(40, 30),
C      1 D22(40, 30), D12(40, 30), SUMC(40, 30, 3), COUNT(40, 30), VX(41, 31),
C      * VZ(41, 31), CONC(40, 30, 3), XIMEQ(15, 3, 3), CBMEQ(5, 5), SEL(5, 5),
C      * DISP(40, 30), CEC(40, 30, 3), XMEQ(40, 30, 3, 3), DISPT(5), CECI(15, 3),
C      2 XPOS(6000), ZPOS(6000), CON(6000, 3), RHOI(5), PORI(15),
C      * DIL(15), DIT(15), BULKI(15), VIX(15), VIZ(15), TITLE(20),
C      * CIMMOL(5), CRAK(5), CHG(5), ION(5), IEX(5),
C      3 NOUP(30), IPX(5), IPZ(5), MF(30)
C      INTEGER*2 ICOH(40, 30)
C      DATA LCR, LLP, KFLAG, TIME, ME/5.6, 0.0, 0/
C
C      Set up starting conditions for the simulation grid
C

```

```

401 C
402 READ(LCR,100)TITLE
403 100 FORMAT(20A4)
404 WRITE(LLP,100)TITLE
405 READ(LCR,200)NR,NC,NPER,NLB,NRB,KTOTAL,MEW
406 WRITE(LLP,200)NR,NC,NPER,NLB,NRB,KTOTAL,MEW
407 200 FORMAT(7I5)
408 READ(LCR,300) (NOUP(J),J=1,NC)
409 WRITE(LLP,300) (NOUP(J),J=1,NC)
410 300 FORMAT(24I3)
411 NCA=NC-1
412 NRA=NR-1
413 READ(LCR,400) DELX,DELZ,DELT,ALPHA,DAVG
414 WRITE(LLP,101) DELX,DELZ,DELT,ALPHA,DAVG
415 101 FORMAT(8F7.2)
416 400 FORMAT(8F10.2)
417 C
418 C Input chemical data
419 C
420 READ(LCR,500)NEX,NUNIT,NION,NEOIL,TOL
421 500 FORMAT(4I5,1E10.3)
422 WRITE(LLP,201)NION,NEOIL,TOL
423 201 FORMAT(//,20X,'SUMMARY OF CHEMICAL DATA',/)
424 1 5X,'NUMBER OF AQUEOUS SPECIES',4X,15/
425 2 5X,'NUMBER OF EQUIL RELATIONSHIPS',1X,15/
426 3 5X,'TOLERANCE FOR ITERATIONS',3X,E13.6)
427 C
428 C Input the transport parameters and layout
429 C the spatial variability code
430 C
431 DO 315 K=1,NUNIT
432 READ(LCR,600)ID,BULK1(K),PORI(K),DIL(K),DIT(K),VIZ(K),VIX(K)
433 * (CECI(K,KK),KK=1,NEX)
434 WRITE(LLP,600)ID,BULK1(K),PORI(K),DIL(K),DIT(K),VIZ(K),VIX(K)
435 * (CECI(K,KK),KK=1,NEX)
436 315 CONTINUE
437 600 FORMAT(15,9F10.3)
438 WRITE(LLP,301)
439 301 FORMAT(//,20X,'INIT MILLIEQUIV/100G ON EXCHANGERS',/)
440 * 7X,'ION',6X,'UNIT',6X,'EXCH 1,2,...,NEX',/)
441 DO 147 K3=1,NION
442 DO 147 K1=1,NUNIT
443 READ(LCR,700) IOP,ID,(XIMEO(K1,K2,K3),K2=1,NEX)
444 WRITE(LLP,401)IOP,ID,(XIMEO(K1,K2,K3),K2=1,NEX)
445 147 CONTINUE
446 700 FORMAT(1A5,15,10F5.2)
447 401 FORMAT(5X,1A5,5X,15,5X,10F5.2)
448 WRITE(LLP,501)
449 501 FORMAT(//,20X,' SPATIAL VARIABILITY CODE',/)
450 DO 235 K=1,NR
1-NR-K+1

```



```

501 DO 259 K=1,NION
502 XMEQ(I,J,K,K)=XMEQ(ID,K,K)
503
504 259 CONTINUE
505
506 DO 310 J=1,NC
507 MF(J)=0
508 DO 310 I=1,NR
509 CAVG(I,J)=0.0
510 DELC(I,J)=0.0
511 DO 310 KK=1,NION
512 CONC(I,J,KK)=CBAK(KK)
513 DELB(I,J,KK)=1.0
514
515 310 CONTINUE
516
517 DO 311 J=1,NC
518 DO 311 KK=1,NION
519 CONC(NIUP(J),J,KK)=CBAK(KK)
520 IF(J.GE.NLB.AND.J.LT.NRB)CONC(NIUP(J),J,KK)=CTIMMOL(KK)
521
522 311 CONTINUE
523
524 C Calculate velocities and dispersion coefficients
525
526 NAT=0
527 DO 107 I=1,NR
528 DO 107 J=1,NC
529 COUNT(I,J)=0.0
530 IF(VX(I,J).EQ.0.0.AND.VZ(I,J).EQ.0.0) GO TO 204
531 IF(J.EQ.1.OR.J.EQ.NC)GO TO 204
532
533 C If velocity contrast between layers is too great,
534 substitute:
535 VX = VX(I,J)
536 VZ = VZ(I,J)
537
538 .....
539
540 for:
541 .....
542 VX = .25*(VX(I,J)+VX(I,J+1)+VX(I+1,J)+VX(I+1,J+1))
543 VZ = .25*(VZ(I,J)+VZ(I,J+1)+VZ(I+1,J)+VZ(I+1,J+1))
544 .....
545
546 IF(I.EQ.NIUP(J)) VZ=VZ(I,J)
547 VXX=VZ(I,J)
548 VZZ=VZ(I,J)
549 IF(NAT.EQ.0) GO TO 206
550 VC2 = SORT(VXX**2+ VZZ**2)
551 GO TO 207
552
553 206 NAT = 1
554 VC1=VZ(I,J)
555 VC1=VZ(I,J)

```

```

551 VMAX=VC1
552 GO TO 208
553 IF (VC2.GT.VC1) VMAX=VC2
554 VC1=VC2
555 VELX =VXX*VXX
556 VELZ =VZZ*VZZ
557 VEL =SQRT(VELX+VELZ)
558 DT=DISP(1,J)*VEL
559 DL=DISP(1,J)*VEL
560 D11(1,J)=(DL*VXX*VXX)/(VEL*VEL)+(DT*VZZ*VZZ)/(VEL*VEL)
561 D22(1,J)=(DL*VXX*VXX)/(VEL*VEL)+(DL*VZZ*VZZ)/(VEL*VEL)
562 D12(1,J)=-(DL*DT)*VXX*VZZ/(VEL*VEL)
563 GO TO 107
564 D11(1,J)=0.0
565 D22(1,J)=0.0
566 D12(1,J)=0.0
567 107 CONTINUE
568 DO 105 I=1,NRR
569 VX(1,I)=0.0
570 VZ(1,I)=0.0
571 VX(1,NC+1)=0.0
572 VZ(1,NC+1)=0.0
573 DO 106 J=1,NCC
574 VX(1,J)=0.0
575 VZ(1,J)=0.0
576
577 C Add points to grid initially
578 C
579 NP=0
580 IT=0
581 CALLADD(NOUNP,MF,SUMC,COUNT,XPOS,ZPOS,CON,CBAK,CIMMOL)
582 IT=1
583
584 C Calculate mass transport through dispersion of particles
585 C
586 DO 112 J=1,NC
587 IA= NOUNP(J)
588 DO 112 I=1,IA
589 COUNT(I,J)=0.0
590 DO 112 KK=1,NION
591 SUMC(I,J,KK)=0.0
592 XMAX= FLOAT(NC)*DELX -DELX
593 TIME=TIME+DELT
594 ME=ME+1
595 DO 111 K=1,NP
596 IXE=(XPOS(K)+DELX)/DELX
597 IZE=(ZPOS(K)+DELZ)/DELZ
598
599 C If velocity contrast between layers is too great,
600 C substitute:

```

```

601 C *****
602 C VEX=VX(IZE,IXE)
603 C VEZ=VZ(IZE,IXE)
604 C *****
605 C
606 C for:
607 C *****
608 C XLOCAL=(XPOS(K)+DELX)/DELX-FLOAT(IXE)
609 C ZLOCAL=(ZPOS(K)+DELZ)/DELZ-FLOAT(IZE)
610 C XELX1= VX(IZE,IXE)+XLOCAL*(VX(IZE,IXE+1)-VX(IZE,IXE-1))
611 C XELX2= VX(IZE+1,IXE)+XLOCAL*(VX(IZE+1,IXE+1)-VX(IZE+1,IXE))
612 C VEX = XELX1+ZLOCAL*(XELX2-XELX1)
613 C ZELX1=VZ(IZE,IXE)+ZLOCAL*(VZ(IZE+1,IXE)-VZ(IZE,IXE))
614 C ZELX2=VZ(IZE,IXE+1)+ZLOCAL*(VZ(IZE+1,IXE+1)-VZ(IZE,IXE+1))
615 C VEZ = ZELX1+XLOCAL*(ZELX2-ZELX1)
616 C *****
617 C
618 C
619 C XPOS(K)=XPOS(K)-DELT*VEX
620 C ZPOS(K)=ZPOS(K)-DELT*VEZ
621 C IF (KAY.EQ.1) GO TO 245
622 C KK=KAY-1
623 C DO 243 I=1,KK
624 C IF (XPOS(K).LE.FLOAT(IPX(I))*DELX-3.0*DELX/2.0.OR.XPOS(K).GE.
625 C 1*FLOAT(IPX(I))*DELX+DELX/2.0) GO TO 243
626 C IF (ZPOS(K).GT.FLOAT(IPZ(I))*DELZ-3.0*DELZ/2.0.AND.ZPOS(K).LT.
627 C 1*FLOAT(IPZ(I))*DELZ+DELZ/2.0)GO TO 215
628 C 243 CONTINUE
629 C 245 IF(XPOS(K).LT.DELX.OR.XPOS(K).GT.XMAX) GO TO 215
630 C IXE=(XPOS(K)+DELX)/DELX
631 C IF(ZPOS(K).LT.DELZ.OR.ZPOS(K).GT.FLOAT(NOUP(IXE))*DELZ-DELZ*1.0)
632 C 1GO TO 215
633 C IZE=(ZPOS(K)+DELZ)/DELZ
634 C COUNT(IZE,IXE)=COUNT(IZE,IXE)+1.0
635 C DO 360 KK=1,NION
636 C 360 SUMC(IZE,IXE,KK)=SUMC(IZE,IXE,KK)+CON(K,KK)
637 C GO TO 111
638 C 215 XPOS(K)=-1.0
639 C 111 CONTINUE
640 C
641 C
642 C Remove points outside region
643 C K=1
644 C 218 IF(K.GT.NP)GOTO 216
645 C IF(XPOS(K).GE.0.0)GOTO 217
646 C NP=NP-1
647 C IF(K.GT.NP)GOTO 216
648 C DO 113 J=K,NP
649 C XPOS(J)=XPOS(J+1)
650 C ZPOS(J)=ZPOS(J+1)

```



```

651      DO 361 KK=1,NION
652      361 CON(J,KK)=CON(J+1,KK)
653      113 CONTINUE
654      K=K-1
655      217 K=K+1
656      GOTO 218
657
658      C
659      C Add necessary particles
660      C
661      216 CALLADD(NOUNP,MF,SUMC,COUNT,XPOS,ZPOS,CON,CBAK,CIMMOL)
662      C
663      C Calculate cell concentration after particle motion
664      C
665      DO 222 J=2,NCA
666      IA=NOUNP(J)
667      DO 222 I=2,IA
668      IF(COUNT(I,J).EQ.O)GO TO 222
669      DO 362 KK=1,NION
670      362 CONC(I,J,KK)=SUMC(I,J,KK)/COUNT(I,J)
671      222 CONTINUE
672
673      C
674      C Account for ion exchange
675      C
676      DO 430 J=2,NCA
677      IA=NOUNP(J)-1
678      DO 430 I=2,IA
679      DO 430 KK=1,NION
680      430 DELB(I,J,KK)=1.O
681      DO 431 J=2,NCA
682      IA=NOUNP(J)-1
683      DO 431 I=2,IA
684      IF(CONC(I,J,1).LT.TOL*50.)GO TO 431
685      BUDPOR=BULK(I,J)/POR(I,J)
686      CALL CATX(I,J,CONC,CEC,XMEQ,CHG,SEL,BUDPOR,TOL,DELB)
687      431 CONTINUE
688      DO 433 J=2,NCA
689      DO 433 KK=1,NION
690      433 CONC(NOUNP(J),J,KK)=CONC(NOUNP(J)-1,J,KK)
691      IXE=(XPOS(K)+DELX)/DELX
692      IZE=(ZPOS(K)+DELZ)/DELZ
693      DO 432 KK=1,NION
694      432 CON(K,KK)=CON(K,KK)*DELB(IZE,IXE,KK)
695
696      C
697      C Solve the diffusion equation
698      C
699      DO 363 KK=1,NION
700      DO 365 J=2,NCA
701      IA=NOUNP(J)
702      DO 365 I=2,IA

```

```

701 365 CAVG(I,J)=CONC(I,J,KK)
702 CALL SOLVE(NOUNP,CAVG,D11,D22,D12,RHO,POR,DELC)
703 DO 120 J=2,NCA
704   IA=NOUNP(J)-1
705   DO 120 I=2,IA
706     DELB(I,J,KK)=DELC(I,J)
707     CAVG(I,J,KK) = CAVG(I,J)+DELC(I,J)
708 363 CONTINUE
709   DO 268 K=1,NP
710     IXE=(XPOS(K)+DELX)/DELX
711     IZE=(ZPOS(K)+DELZ)/DELZ
712     DO 268 KK=1,NION
713       CON(K,KK)=CON(K,KK)+DELB(IZE,IXE,KK)
714 268 CONTINUE
715 C
716 C Account for ion exchange
717 C
718   DO 429 J=2,NCA
719     IA=NOUNP(J)-1
720     DO 429 I=2,IA
721       DO 429 KK=1,NION
722         DELB(I,J,KK)=1.0
723   429 DELB(I,J,KK)=1.0
724     DO 426 J=2,NCA
725       IA=NOUNP(J)-1
726       DO 426 I=2,IA
727         IF(CONC(I,J,1).LT.TOL*50.)GO TO 426
728         BUDPOR-BULK(I,J)/POR(I,J)
729         CALL CATX(I,J,CONC,CEC,XMEQ,CHG,SEL,BUDPOR,TOL,DELB)
730 426 CONTINUE
731   DO 427 K=1,NP
732     IXE=(XPOS(K)+DELX)/DELX
733     IZE=(ZPOS(K)+DELZ)/DELZ
734     DO 427 KK=1,NION
735       CON(K,KK)=CON(K,KK)+DELB(IZE,IXE,KK)
736 427 CON(K,KK)=CON(K,KK)+DELB(IZE,IXE,KK)
737 C
738 C Output the average concentration for current time interval
739 C
740   IF(ME.EQ.MEM) GO TO 277
741   GO TO 278
742 277 ME=O
743   YEAR=TIME
744   WRITE(LLP,901)YEAR
745   901 FORMAT(1H1,/,TIME=,3X,IF16.1,2X,'YEARS')
746   KOP=NOUNP(1)
747   DO 121 IA=1,KOP
748     I=KOP-IA+1
749     WRITE(LLP,1001)(CONC(I,J,1),J=2,NCA)
750 121 CONTINUE
751   WRITE(LLP,1101)
752   1101 FORMAT(////)

```

```

751 DO 420 IA=1,KOP
752 I=KOP-IA+1
753 WRITE(LLP,1001)(CONC(I,J,2),J=2,NCA)
754
755 420 CONTINUE
756 WRITE(LLP,1101)
757 DO 422 IA=1,KOP
758 I=KOP-IA+1
759 WRITE(LLP,1001)(CONC(I,J,3),J=2,NCA)
760
761 422 CONTINUE
762 1001 FORMAT(15F8.4)
763 278 KFLAG = KFLAG+1
764 IF(KFLAG.EQ.KTOTAL)GO TO 231
765 GO TO 230
766
767 231 STOP
768 END
769
770 C Subroutine SOLVE
771 C
772 SUBROUTINE SOLVE(NOUNP,CAVG,D11,D22,D12,RHO,POR,DELX)
773 COMMON ALPHA,DAVG,DELX,DELZ,DELT,
774 * NCA,NP,NPER,IT,NLB,NRB,NEX,NION,NEQIL
775 DIMENSION CAVG(40,30),RHO(40,30),POR(40,30),DELX(40,30),
776 * D11(40,30),D22(40,30),D12(40,30),NOUNP(30)
777
778 C Solve the dispersion equation
779 C
780 DO 119 J=2,NCA
781 IA=NOUNP(J)-1
782 DO 119 I=2,IA
783 W=RHO(I,J)/(RHO(I,J)-(ALPHA*DAVG))
784 IF(D11(I,J+1).EQ.0.0.OR.D11(I,J).EQ.0.0) GO TO 31
785 DCXA=((2.0*W*POR(I,J+1)*DELT*D11(I,J+1))/(DELX*DELX+
786 1(POR(I,J)*D11(I,J)+POR(I,J+1)*D11(I,J+1)))*(CAVG(I,J+1)-CAVG(I,J
787 2)))
788 GO TO 32
789 31 DCXA=0.0
790 32 IF(D11(I,J-1).EQ.0.0.OR.D11(I,J).EQ.0.0) GO TO 33
791 DCXB=((2.0*W*POR(I,J-1)*DELT*D11(I,J-1))/(DELX*DELX+
792 1(POR(I,J)*D11(I,J)+POR(I,J-1)*D11(I,J-1)))*(CAVG(I,J)-CAVG(I,J-1
793 2)))
794 GO TO 34
795 33 DCXB=0.0
796 34 IF(D22(I+1,J).EQ.0.0.OR.D22(I,J).EQ.0.0) GO TO 35
797 DCYC=((2.0*W*POR(I+1,J)*DELT*D22(I,J+1))/(DELZ*DELZ+
798 1(POR(I,J)*D22(I,J)+POR(I+1,J)*D22(I+1,J)))*(CAVG(I+1,J)-CAVG(I,J
799 2)))
800 GO TO 36
801 35 DCYC=0.0
802 36 IF(D22(I-1,J).EQ.0.0.OR.D22(I,J).EQ.0.0) GO TO 37
803 DCYD=((2.0*W*POR(I-1,J)*DELT*D22(I,J-1))/(DELZ*DELZ+

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```

801      1(POR(I,J)*D22(I,J)+POR(I-1,J)*D22(I-1,J)))+(CAVG(I,J)-CAVG(I-1,J
802      2))
803      GO TO 38
804      37 DCYVD=0.0
805      38 IF(D12(I,J+1).EQ.0.0.OR.D12(I,J).EQ.0.0) GO TO 39
806      DCXYA=((W*POR(I,J+1)*DELTD12(I,J)*D12(I,J+1))/(2.0*DELX*DELZ*
807      1(POR(I,J)*D12(I,J)+POR(I,J+1)*D12(I,J+1)))+(ABS(CAVG(I+1,J+1)-CAV
808      2G(I-1,J+1)-CAVG(I-1,J)+CAVG(I+1,J)))
809      GO TO 40
810      39 DCXYA=0.0
811      40 IF(D12(I,J-1).EQ.0.0.OR.D12(I,J).EQ.0.0)GO TO 41
812      DCXYB=((W*POR(I,J-1)*DELTD12(I,J)*D12(I,J-1))/(2.0*DELX*DELZ*
813      1(POR(I,J)*D12(I,J)+POR(I,J-1)*D12(I,J-1)))+(ABS(CAVG(I+1,J)-CAVG(
814      2I-1,J)-CAVG(I-1,J-1)+CAVG(I+1,J-1)))
815      GO TO 42
816      41 DCXYB=0.0
817      42 IF(D12(I+1,J).EQ.0.0.OR.D12(I,J).EQ.0.0) GO TO 43
818      DCXYC=((W*POR(I+1,J)*DELTD12(I,J)*D12(I+1,J))/(2.0*DELX*DELZ*
819      1(POR(I,J)*D12(I,J)+POR(I+1,J)*D12(I+1,J)))+(ABS(CAVG(I+1,J+1)-CAV
820      2G(I+1,J-1)-CAVG(I,J-1)+CAVG(I,J+1)))
821      GOT044
822      43 DCXYC=0.0
823      44 IF(D12(I-1,J).EQ.0.0.OR.D12(I,J).EQ.0.0)GO TO 45
824      DCYXD=((W*POR(I-1,J)*DELTD12(I,J)*D12(I-1,J))/(2.0*DELX*DELZ*
825      1(POR(I,J)*D12(I,J)+POR(I-1,J)*D12(I-1,J)))+(ABS(CAVG(I,J+1)-CAVG(
826      2I,J-1)-CAVG(I-1,J-1)+CAVG(I-1,J+1)))
827      GO TO 46
828      45 DCYXD=0.0
829      46 SA=CAVG(I+1,J+1)+CAVG(I-1,J+1)-CAVG(I-1,J)-CAVG(I+1,J)
830      SB=CAVG(I-1,J)+CAVG(I+1,J)-CAVG(I-1,J-1)-CAVG(I+1,J-1)
831      SC=CAVG(I+1,J+1)+CAVG(I+1,J-1)-CAVG(I,J+1)-CAVG(I,J-1)
832      SD=CAVG(I,J+1)+CAVG(I,J-1)-CAVG(I-1,J+1)-CAVG(I-1,J-1)
833      IF(SA.EQ.0.0)GO TO 325
834      SA=SA/ABS(SA)
835      IF(SB.EQ.0.0) GO TO 326
836      SB=SB/ABS(SB)
837      IF(SC.EQ.0.0) GO TO 327
838      SC=SC/ABS(SC)
839      IF(SD.EQ.0.0) GO TO 328
840      SD=SD/ABS(SD)
841      328 DELC(I,J)=DCXXA-DCXXB+DCYYC-DCYYD+DCXYA*SA-DCXYB*SB
842      1+DCYXC*SC-DCYXD*SD
843      119 CONTINUE
844      RETURN
845      END
846
847      C Subroutine ADD
848      C
849      SUBROUTINEADD(NOUNP,MF,SUMC,COUNT,XPOS,ZPOS,CON,CBAK,CIMMOL)
850      COMMON ALPHA,DAVG,DELX,DELZ,DELT.

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851      NCA,NP,NPER,IT,NLB,NRB,NEX,NION,NEQIL
852      DIMENSION NOUP(30),COUNT(40,30),XPOS(6000),ZPOS(6000),
853      *      CON(6000,3),SUMC(40,30,3),MF(30),CBAK(5),CMMOL(5)
854      DO 108 J=2,NCA
855      IA = NOUP(J)-1
856      DO 108 I=2,IA
857      IF(IX(COUNT(I,J)),GE NPER)GO TO 108
858      NRA=NPER-IFIX(COUNT(I,J))
859      IF(IT.EQ.O)GO TO 200
860      IF(I.NE.IA)GO TO 108
861      DO 109 K=1,NRA
862      NP=NP+1
863      MF(J)=MF(J)+1
864      IF(MF(J).GT.NPER)MF(J)=1
865      XPOS(NP)=FLOAT(J)*DELX-DELX*MF(J)*DELX/FLOAT(NPER+1)
866      ZPOS(NP)=FLOAT(I)*DELZ-.00005*DELZ
867      DO 280 KK=1,NION
868      CON(NP,KK)=CBAK(KK)
869      IF(J.GE.NLB.AND.J.LT.NRB)CON(NP,KK)=CMMOL(KK)
870      280 SUMC(I,J,KK)=SUMC(I,J,KK)+CON(NP,KK)
871      109 CONTINUE
872      COUNT(I,J)= NPER
873      GO TO 108
874      DO 110 K=1,NRA
875      NP=NP+1
876      IF(I.EQ.IA)GO TO 209
877      XPOS(NP)=FLOAT(J)*DELX-DELX*(FLOAT(K)/(FLOAT(NPER)+1))*DELX
878      ZPOS(NP)=FLOAT(I)*DELZ-(FLOAT(K)/(FLOAT(NPER)+1))*DELZ
879      DO 285 KK=1,NION
880      CON(NP,KK)=CBAK(KK)
881      GO TO 110
882      209 XPOS(NP)=FLOAT(J)*DELX-DELX*(FLOAT(K)/(FLOAT(NPER)+1))*DELX
883      ZPOS(NP)=FLOAT(I)*DELZ-DELX*DELZ+DELZ*FLOAT(K)/FLOAT(NPER)
884      DO 290 KK=1,NION
885      CON(NP,KK)=CBAK(KK)
886      IF(K.EQ.NPER.AND.J.GE.NLB.AND.J.LT.NRB)CON(NP,KK)=CMMOL(KK)
887      290 CONTINUE
888      110 CONTINUE
889      108 CONTINUE
890      RETURN
891      END
892
893      C      Subroutine CATEX
894      C
895      SUBROUTINE CATEX(ICELL,JCELL,CONC,CEC,XMEQ,CHG,SEL,BUDPOR
896      1      ,TOL,DELB)
897      COMMON ALPHA,DAVG,DELX,DELZ,DELT,
898      *      NCA,NP,NPER,IT,NLB,NRB,NEX,NION,NEQIL
899      REAL*8 CTMASS(5),DELM(5),CBMEQ(5,5),
900      *      CBMMOL(5,5),XT(5,5),XM(5,5),CMMOL(5),STN(5),..

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```

901      * SINP(5),CTEST(5),CP,DIF
902      * DIMENSION CONC(40,30,3),CEC(40,30,3),XMEQ(40,30,3),CHG(5),
903      * DELB(40,30,3),SEL(5,5),CT(5)
904      990 FORMAT(10I5)
905      991 FORMAT(10F10,4)
906
907      C Initialize ion concentration in each cell
908      C
909      DO 210 I=1,NION
910      CMHOL(1)=CONC(ICELL,JCELL,I)
911      CT(I)=CMHOL(1)
912      210 CONTINUE
913
914      C Calculate initial concentration on exchanger
915      C
916      DO 213 I=1,NEX
917      DO 213 J=1,NION
918      CBMEQ(I,J)=XMEQ(ICELL,JCELL,I,J)
919      CBMMOL(I,J)=CBMEQ(I,J)*BUDPOR/(CHG(J)/10.)
920      213 CBMMOL(I,J)=CBMEQ(I,J)*BUDPOR/(CHG(J)/10.)
921
922      C Sum up total amount of mass in system
923      C
924      DO 214 J=1,NION
925      CTMASS(J)=CT(J)
926      DO 216 I=1,NEX
927      CTMASS(J)=CTMASS(J)+CBMMOL(I,J)
928      {CT=0
929      DELM(1)=CT(1)/2.
930      DELM(2)=CT(2)/3.
931      DELM(3)=CT(2)/2.
932      DO 250 J=1,NION
933      SINP(J)=-1.0
934      999 ICT=ICT+1
935
936      C Calculate ion exchange
937      C
938      DO 218 I=1,NEX
939      XT(I,1)=1.0
940      XT(I,2)=CMHOL(2)/(SEL(I,1)+CMHOL(1))
941      XT(I,3)=CMHOL(3)/(CMHOL(1)+SEL(I,2))
942      XM(I,1)=1.0
943      XM(I,2)=CMHOL(1)*SEL(I,1)/CMHOL(2)
944      XM(I,3)=CMHOL(3)/(CMHOL(2)+SEL(I,3))
945      DO 215 I=1,NEX
946      CBMEQ(I,1)=CEC(ICELL,JCELL,I)/(XT(I,1)+XT(I,2)+XT(I,3))
947      CBMEQ(I,2)=CEC(ICELL,JCELL,I)/(XM(I,1)+XM(I,2)+XM(I,3))
948      CBMEQ(I,3)=CEC(ICELL,JCELL,I)-CBMEQ(I,1)-CBMEQ(I,2)
949      215 CBMEQ(I,3)=CEC(ICELL,JCELL,I)-CBMEQ(I,1)-CBMEQ(I,2)
950
951      C Convert concentration on exchanger from

```

```

951 C meq/100g to mmol
952 C
953 DO 220 I=1,NEX
954 CBMMOL(1,1)=CBMEQ(1,1)*BUDPOR/(CHG(4)/10.)
955 CBMMOL(1,2)=CBMEQ(1,2)*BUDPOR/(CHG(2)/10.)
956 CBMMOL(1,3)=CBMEQ(1,3)*BUDPOR/(CHG(3)/10.)
957 C
958 C Recalculate the concentration in solution
959 C
960 DO 235 J=1,NION
961 CTEST(J)=CTMASS(J)
962 DO 236 J=1,NION
963 DO 236 I=1,NEX
964 CTEST(J)=CTEST(J)-CBMMOL(I,J)
965 DO 245 J=1,NION
966 IF(CTEST(J).GT.CMMOL(J)) SIN(J)=1.0
967 IF(CTEST(J).LE.CMMOL(J)) SIN(J)=-1.0
968 IF(SIN(J).NE.SINP(J)) DELM(J)=DELM(J)/2.0
969 IF(CMMOL(J).EQ.DELEM(J))DELM(J)=DELM(J)/2.0
970 SINP(J)=SIN(J)
971 CMMOL(J)=CMMOL(J)+SIN(J)*DELM(J)
972 C
973 C Check TOL for convergence
974 C
975 DIF=1000.
976 IF(1CT.GT.1) DIF=DABS(CMMOL(1)-CP)
977 CP=CMMOL(1)
978 IF(1CT.EQ.100) GO TO 998
979 IF(DIF.GT.TOL)GO TO 999
980 IF(1CT.EQ.60)WRITE(6,100)DIF
981 DO 230 J=1,NION
982 DELB(ICELL,JCELL,J)=CMMOL(J)/CONC(ICELL,JCELL,J)
983 CONC(ICELL,JCELL,J)=CMMOL(J)
984 DO 230 I=1,NEX
985 XMEQ(ICELL,JCELL,I,J)=CRMEQ(I,J)
986 100 FORMAT('** ITERATION LIMIT EXCEEDED **',1E10.4)
987 RETURN
988 END
989
990

```